



FIGURE 63.

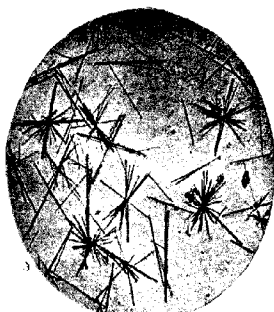


FIGURE 62.

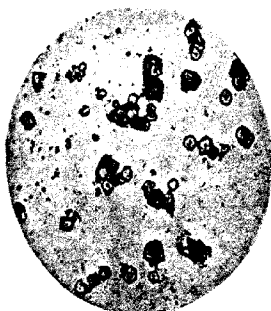


FIGURE 64.



FIGURE 65.

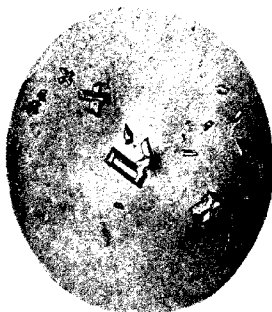


FIGURE 66.



FIGURE 67.

Figure 62. Calcium sulphate crystals magnified twenty diameters.
 Figure 63. Magnesium silicofluoride crystals magnified thirty diameters.
 Figure 64. Cesium aluminum sulphate crystals magnified twenty diameters.
 Figure 65. Ammonium magnesium phosphate crystals magnified ten diameters.
 Figure 66. The same crystallized from dilute solution magnified thirty diameters.
 Figure 67. Ammonium phosphomolybdate crystals magnified 140 diameters.

Magnesium.—Rhombohedral crystals of magnesium silicofluorid separate from the solution of particles containing magnesium in hydrofluosilicic acid. They have the composition $\text{MgSiF}_6 \cdot 6\text{H}_2\text{O}$ and their common forms are shown in Fig. 63. Quite characteristic also are the crystals of struvite, $(\text{NH}_4\text{MgPO}_4 + 6\text{H}_2\text{O})$, which are produced in a very dilute solution of the magnesium compound first obtained by carefully adding ammonium hydroxid and chlorid until a faint alkaline reaction is produced, and then placing a drop of dilute sodium phosphate at the edge of the solution. The crystals should be allowed to form slowly in the cold. Their form is shown in Fig. 65.

Barium.—From solution of fragments of barium-bearing minerals in hydrofluosilicic acid, no characteristic crystals are obtained. Treated with hydrofluoric and sulfuric acids the barium is left as sulfate. If this salt be dissolved in boiling oil of vitriol and a drop of the solution placed on the slide, a mixture of rectangular tablets and St. Andrew's cross-shaped growths will be separated before any crystals of gypsum which may be present appear. When strontium is present, the barium sulfate residue obtained by treatment with hydrofluoric and sulfuric acids should be fused with sodium and potassium carbonate, washed with water until the sulfuric acid is removed, the residue dissolved in hydrochloric or nitric acid, and the solution treated with potassium chromate. Pale yellow crystals of barium chromate are thus obtained, which resemble in form those secured by dissolving the barium sulfate in oil of vitriol. Strontium is not precipitated by this treatment. If potassium ferrocyanid be used instead of barium chromate with the hydrochloric acid solution, crystals of barium potassium ferrocyanid are formed of a bright yellow color and rhombohedral shape.

Strontium.—From a hydrofluosilicic acid solution, strontium crystallizes in columns or tablets of the monoclinic system as strontium silicofluorid, SrSiF_6 . On treating these with sulfuric acid, rhombic plates of strontium sulfate are formed, which serve to distinguish this element from calcium. On treatment of the particles of the original mineral with hydrofluoric and sulfuric

acids, the strontium remains in the insoluble residue. When this residue is treated with boiling oil of vitriol, rhombic plates of celestine are separated. If the residues above mentioned be dissolved by fusion with the alkaline carbonates, washed with water, dissolved in hydrochloric acid and treated with oxalic acid, octahedral crystals of strontium oxalate are formed.

Iron.—Mineral particles containing iron give crystals, when treated as is first described above, which are fully isomorphous with those obtained from magnesium. By moistening the crystalline mass with potassium ferrocyanid, the presence of iron is at once revealed by the blue coloration produced.

Aluminum.—No crystals containing aluminum are formed from the mineral particles containing this substance when dissolved in the solvent already mentioned. If, however, the gelatinous mass be dissolved in a little sulfuric acid and a fragment of a cesium salt added, beautiful crystals of cesium alum are obtained, illustrated in Fig. 64.

Phosphorus.—When a mineral fragment containing phosphorus is treated according to the usual analytical methods for securing the ammonium magnesium phosphate, crystals are obtained of the form shown in Figs. 65 and 66. A phosphatic fragment of silt may be identified when soluble by treatment with nitric acid and ammonium molybdate. On slowly drying, rhombohedral crystals are produced, yellow by reflected, and green by transmitted light. Their form is shown in Fig. 67.

290. Petrographic Examination of Silt Particles.—The larger silt particles and the minute fragments of minerals in the soil can best be studied in thin sections. For this purpose the following plan, proposed by Thoulet, may be used.⁴ Mix the soil minerals in considerable proportion—Thoulet recommends ten per cent, but a greater percentage is often better—with zinc oxid and make into a paste with sodium silicate. The paste should be worked to the consistence of putty and then rolled into little tablets about one-eighth of an inch thick and an inch in diameter. After drying a day or two without heating, the tablets become hard enough

⁴ Contributions à l'Étude des Propriétés physiques et chimiques des minéraux microscopiques, Paris, 1880 : 64 et seq.

to mount and grind like rock sections. These tablets are mounted in canada balsam on glass slides and ground as thin as possible with fine emery on the turn-table or glass plate, as rock sections are treated. As these tablets are not as strong as rock sections usually are, they require care in this treatment. Some of the grains also are apt to be torn out in the process of grinding and to compensate for this loss a number of slides should be prepared with each lot of soil minerals. When this operation has been successful, the optical properties of the various minerals can be studied as in rock sections.

As the iron oxid contained in the soils obscures the transparency of the minerals, it is well to treat a portion of the material under examination with hot hydrochloric acid for a short time to remove this oxid and then prepare slides with the cleansed material and compare results with the untreated. As the acid will dissolve phosphates and carbonates, and will partly or wholly decompose some other minerals, the operator must be guided by his judgment in its use.

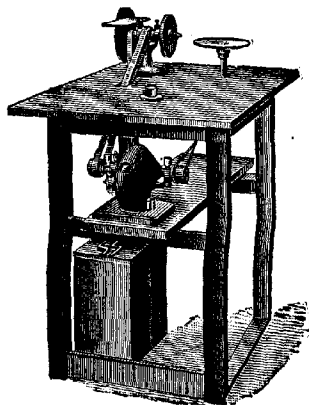


Fig. 68. Machine for Making Mineral Sections.

291. **Machine for Making Mineral Sections.**—A convenient apparatus for this purpose has been described by Williams⁵ and is represented in Fig. 68. It is supported on a substantial table pro-

⁵ American Journal of Science, 1893, 37, 45 : 103.

vided underneath with electric batteries and a motor for driving the cutting disks seen on the top. The table is three feet six inches square and two feet nine inches high.

The grinding apparatus consists of two circular disks of solid copper, nine inches in diameter, and three-eighths inch thick, which may be used alternately as different grades of emery are required. They are attached either by a screw or square socket to a vertical iron spindle which revolves smoothly in a conical bearing. The grinding disk is surrounded when in use by a large cylindrical pan of tin, which is not shown in the cut, which has an opening in its center to allow of the passage of the spindle.

The sawing apparatus consists of a horizontal countershaft placed on a different part of the table and connected with the motor by a separate belt. It carries at one end a vertical wheel of solid emery, and at the other an attachment, level-table and guide for the diamond-saw. A small water-can with spout, not shown in the cut, is suspended over the edge of the table to keep the saw wet when it is in use.

The machine is very conveniently driven by a storage battery when street circuits cannot be drawn on.

For the details of making mineral sections, the works on petrography may be consulted.

292. Separation of Silt Particles by Specific Gravity Solutions.—In silt separates the specific gravity of the different mineral particles present may vary from graphite (1.9—2.3) to hematite (5.2—5.3).

The following list gives the specific gravities of some of the more common minerals which may be met with in soils:

Gypsum	2.31
Albite	2.56-2.63
Quartz	2.65
Talc	2.74
Chlorite	2.78
Muscovite	2.85
Calcite	2.5 -2.78
Dolomite	2.90
Tourmaline	2.94-3.3
Biotite	3.01
Apatite	3.16
Pyroxenes	3.22-3.5
Epidote	3.39
Titanium minerals	3.48-4.75
Iron oxids	5.2 -5.3

The finest particles of silt are separated by gravity with great difficulty, inasmuch as they tend to remain suspended in the solutions for an indefinite period. With the coarser silts, however, useful data are often obtained by this method. The separation is preceded by extraction of the particles with hydrochloric acid to remove encrusted soluble matter, and by ignition to destroy any traces of organic matter. Those mineral matters which are soluble in acid or are changed by ignition must, of course, be sought for in separate portions of the silt.

293. Thoulet's Solution.⁶—The standard solution which was originally proposed by Sonstadt⁷ is of such a density that particles of 2.65 specific gravity will just float thereon, using for this purpose a solution of about 2.7 specific gravity. The solution from which the above standard is prepared is made as follows:

One part of potassium iodid is placed in a beaker and one and one-quarter parts of mercuric iodid is placed on top of it. Then water is added in the proportion of ten cubic centimeters to 100 grams of the mixture, and after some time (12 to 24 hours), with occasional stirring, the salts will nearly completely dissolve. Filter from the undissolved residue and evaporate in a porcelain dish until crystals form on the surface of the liquid. Allow to cool, pour off the liquid from the crystals and evaporate the liquid for another crop. The first solution, after cooling, has a specific gravity between 3.10 and 3.20, the second a specific gravity of 3.28, practically the limit of density of the solution. The solution of 2.7 specific gravity and other densities are made by cautiously adding a few drops of water at a time and ascertaining the specific gravity by the Westphal balance or other convenient method.

The strong solution, according to Goldschmidt, may be prepared directly by using potassium iodid and mercuric iodid in the ratio of 1:1.24. *Twenty-five cubic centimeters of water, 210 grams of potassium iodid, and 260 grams of mercuric iodid affords a solution of 3.196 specific gravity at 15°, on which fluor-spar fragments will float. If the correct preparation of the two*

⁶ Rosenbusch, *Mikroskopische Physiographie* : 231.

⁷ *Chemical News*, 1874, **29** : 127.

salts be maintained the solution can be diluted with water or concentrated by evaporation without losing its clear deep green color.

294. Klein's Separating Liquid.—A solution of cadmium borotungstate, of the composition $2\text{H}_2\text{O}_2\cdot 2\text{CdO}_2\cdot \text{B}_2\text{O}_3\cdot 9\text{WO}_3 + 16\text{H}_2\text{O}$, has been proposed by Klein⁸ for separating silt particles. This salt is obtained by dissolving pure sodium tungstate in five times its weight of water, adding one and a half parts of boric acid and boiling until complete solution takes place. On cooling, the borax is separated in crystalline form. The mother-liquor after the removal of the crystals is carefully concentrated by boiling. By stirring the cold solution, there is a further separation of sodium borate and polyborate. This operation is continued until glass will float on the mother-liquor. The salt in solution then has the following composition: $4\text{Na}_2\text{O}\cdot 12\text{WO}_3\cdot \text{B}_2\text{O}_3$. To this boiling concentrated solution, is added a boiling saturated solution of barium chlorid, in the proportion of one part of the chlorid to three parts of the original double tungstate. An abundant pulverulent precipitate is formed, making the whole mass mushy. The mass is filtered under pressure and well-washed with hot water. The residue is then suspended in hot water containing one part in ten of hydrochloric acid of 1.18 specific gravity. It is then evaporated to dryness in the presence of an excess of hydrochloric acid and decomposed, by which process hydrated tungstic acid is separated. The boiling mass is taken up with water and the boiling continued for two hours with occasional addition of water to take the place of that evaporated, and the tungstic acid separated by filtration.

From the solution, beautiful quadratic crystals separate having the composition $9\text{WO}_3\cdot \text{B}_2\text{O}_3\cdot 2\text{BaO}_2\cdot \text{H}_2 + 18\text{H}_2\text{O}$. These are purified by several recrystallizations and freed from any scales of boric acid by washing with alcohol. Any reducing action, revealed by a violet coloration of the crystals, can be avoided by adding a few drops of nitric acid. From a boiling solution of these crystals, the cadmium salt desired is obtained by treatment with the proper amount of cadmium sulfate solution to precipitate the barium. The barium sulfate is separated by filtration.

⁸ Comptes rendus, 1881, 93 : 318.

The cadmium borotungstate is soluble in less than ten parts by weight of water. From this solution it is obtained in pure form by evaporation under a vacuum, or by carefully concentrating on a water-bath and cooling. A saturated solution of these crystals at 15° has a bright yellow color and a specific gravity of 3.28.

If a dilute solution of the above salt be carefully evaporated on a water-bath, any violet color which may be present disappears when the specific gravity reaches 2.7. If the evaporation be continued until a crystal of augite will float on the hot liquid, crystals may be obtained on cooling which, dissolved in as little water as possible, make a solution which will almost support olivine. If the two solutions be united, the specific gravity of the mixture is 3.30-3.36. The highest attainable specific gravity; *viz.*, 3.6, is produced by continuing the evaporation on a water-bath until the liquid will support olivine, and then allowing to stand in a closed place for twenty-four hours. The crystals of cadmium borotungstate thus obtained are freed as much as possible from the mother-liquor by drainage and then melted at about 75° in their own water of crystallization. A liquid is thus obtained on which spinel will float. The same concentration may also be obtained by careful heating on a water-bath. At its highest specific gravity this solution has an oily consistence and this renders its practical use in the separation of fine particles somewhat restricted. By filtering the liquor when a crystalline crust begins to form during evaporation, a cold solution of 3.360-3.365 specific gravity is obtained which is found practically useful. It has a higher specific gravity than Thoulet's mixture, is not injurious to any of the mineral particles, not even of iron with which it is brought into contact, but the trouble of preparing it is far greater than that of the mixture of mercuric and potassium iodids.

295. Rohrbach's Solution.—The solution of barium mercuric iodid recommended by Rohrbach⁹ for this purpose was originally prepared by Suchsin, in St. Petersburg. The solution must be rapidly prepared on account of the tendency of the barium salt to decomposition. The solution is prepared by weighing rapidly 100 grams of barium chlorid and 130 grams of mercuric iodid,

⁹ Rosenbusch, *Mikroskopische Physiographie* : 235.

mixing the two salts well in a dry flask and adding 20 cubic centimeters of water. The mixture is raised to a temperature of 150°-200° on an oil-bath. The formation and solution of the double salt are promoted by constant stirring.

After solution, the liquor is boiled for a few minutes and then evaporated on a water-bath until it will bear a crystal of epidote. On cooling, a small quantity of a yellow double salt is separated by crystallization and the resulting mother-liquor is dense enough to carry a fragment of topaz. Inasmuch as the liquor is filtered with difficulty, the clear mother-liquor should be separated by decantation after standing for several days. This solution has the disadvantage of not being dilutable with water, the addition of which causes a separation of red mercuric iodide. Were this solution not so easily decomposed, it would prove of high value in silt separation.

296. Braun's Separating Liquid.—In many respects the separatory solution proposed by Braun¹⁰ is superior to those already mentioned. It is the commercial methylene iodide, CH_2I_2 , which has at 16° a specific gravity of 3.32, at 5° of 3.35, and at 25° of 3.31. It is strongly refractive liquid having an index of 1.7466 for the yellow ray.

As a separating medium the liquid is open to two objections; *viz.*, first, it cannot be diluted with water and, second, it turns brown on heating or on long exposure to the sun-light.

When dilution is necessary, it should be accomplished with benzol or xylol. To bring the diluted liquor again to its maximum density, the benzol must be removed by evaporation, which causes a considerable loss in the liquid. When this substance becomes opaque, the transparency may be restored by removing the separated iodine by shaking with potash lye, washing with pure water, drying by the addition of pieces of calcium chloride and filtering. The same result may also be reached by freezing and separating the liquid portion. The frozen portion on melting will have the density of the original liquid.

297. Separation in Silver and Thallium Nitrates.—A method of separating mineral fragments by means of a heavy solution prepar-

¹⁰ Neues Jahrbuch für Mineralogie, Stuttgart, 1886, II : 72.

ed from silver and thallium nitrates has been described by Penfield.¹¹

This mixture of nitrates was first prepared by Retgers, who showed that when mixed in molecular proportions these nitrates fuse at 75° in the form of a double salt to a clear mobile liquid having a specific gravity of more than 4.5 and capable, while melted of being mixed with water in all proportions.

The separation may be made in an ordinary test tube, while the salts are fused. All the particles heavier than 4.5 specific gravity will sink, and all those lighter float. Very few particles will be found suspended in the liquid. After cooling the tube is broken the solid salt holding the particles of different densities separated, fused and the mineral particles seasoned. Penfield recommends a more elaborate apparatus, the construction and operation of which are described in the paper cited.

298. Method of Breon.—Instead of a solution of a salt, Bréon¹² has proposed to use salts in a fused state for separating mineral particles. Lead and zinc chlorids may be used for this purpose in a melted state, having the specific gravities of 5.0 and 2.4, respectively. By mixing the molten salts in different proportions, any desired specific gravity between the extremes mentioned may be secured. The fusion is accomplished at 400° in a test tube. The silt is added gradually with constant stirring until a sharp separation is secured between the sinking and floating particles. After cooling, the tube is broken, the two parts separated, and the silt recovered by dissolving the mixed salts in hot water containing a little nitric acid. Only the coarser silts can be separated by this method. Fused silver nitrate, melting point 198°, specific gravity 4.1, has also been used for separation.

299. The Separation.—Forty cubic centimeters of the solution in the Thoulet process are placed in the separatory tube A, Fig. 69, together with from one to two grams of the silt and the stopper F inserted. The silt and separatory liquor are well mixed by blowing at I. The cock C is so opened and the blast of air so adjusted that no particles of the silt enter the space between C and

¹¹ American Journal of Science [3], 1895, 50 : 446.

¹² Bulletin, Société minéralogique, 1880, III : 46.

D during this operation. The tube G is connected with a vacuum apparatus by means of which any air particles adhering to the mineral fragments are removed. The silt which sinks in the solution is removed after G has been disconnected by opening the cock C. Any excess of liquid that flows through C during this time is received in the bulb on the tube B. The cock C is closed and the separated particles washed into a beaker at H after opening D. Water is next added to the materials left in A in quantities previously determined to secure a given specific gravity and thus a second, a third, etc., separation secured. An intimate mixture

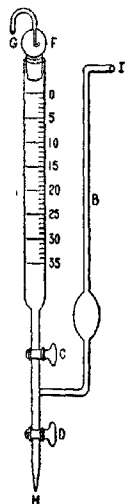


Fig. 69. Thoulet's Separating Apparatus.

of the solutions in A can be effected each time by closing D, opening C, and blowing through B in such a way that no liquid is allowed to pass through C, as already described.

The quantity of water to be added in each case to secure a given specific gravity is determined by the formula

$$v_1 = \frac{v(D - d')}{d - 1},$$

in which v is the volume of the solution, D its specific gravity,

and d and v_1 the specific gravity desired and volume of the water to be added.

Example.—Let the specific gravity of the original solution be 3.2, its volume thirty cubic centimeters, and the desired specific gravity of the new solution 2.85.

$$\text{Then } v_1 = \frac{30(3.2 - 2.85)}{2.85 - 1} = 5.68.$$

The desired specific gravity is therefore secured by adding 5.68 cubic centimeters of water, which is easily accomplished by means of the graduations on the tube.

According to Rosenbusch,¹³ the calculated specific gravity as made above is not wholly reliable on account of the contraction which takes place. An empirical process is rather to be commended which consists in introducing a fragment of mineral of known or desired specific gravity and then adding water drop by drop until the fragment remains suspended in the mixture. Should too much water be added the necessary increase in density can be secured by adding a little of the strong solution.

300. Method of Packard.—A separatory funnel, according to Packard,¹⁴ as suggested by Werveke,¹⁵ may be safely used to hold the solution while separation is going on. As the lighter minerals form the bulk of soils, the heavier constituting only a small percentage, it is well to use a wide funnel holding as much as one-half liter for quantitative separations, because a large quantity of soil, say 100 grams, is necessary from which to recover the small quantity of heavy particles satisfactorily. The soil is introduced into the solution contained in the funnel, agitated, stirred with a glass rod, and allowed to stand some time. This operation may be repeated as often as desired. Separation is not absolute by this operation, the heavy and light particles being sometimes so united that they sink or float together according as one or the other preponderates. There are also particles having so nearly the same specific gravity as the solution that they remain indifferent to its action in any position. After separation has been

¹³ Rosenbusch, *Mikroskopische Physiographie* : 232.

¹⁴ Manuscript communication from R. L. Packard.

¹⁵ *Neues Jahrbuch für Mineralogie*, 1883, II : 86.

effected, the heavy portion is drawn off through the stop-cock of the funnel and the lighter is skimmed off the top. Both must be thoroughly washed from the adhering heavy solution for further examination with the microscope, and by chemical, microchemical, and blow-pipe tests. One who has familiarized himself with the appearance of minerals in minute fragments under the microscope, in ordinary and polarized light, will be able to determine some minerals in that way. But for certain identification it is necessary to ascertain their optical properties as is done in the case of the minerals in thin sections of rocks.

Illustration.—The following example from the work of Packard will serve to illustrate the results of separating a soil by the specific gravity method:

One hundred grams of soil, residual clay from the Trenton limestone, were placed in the Thoulet's solution contained in the large separatory funnel. The heavy portion, after washing and drying, weighed 0.6886 gram, or 0.69 per cent. Of this, the magnet removed 0.1635 gram, or 0.16 per cent. This heavy material consisted of rounded yellowish and brown grains up to twenty-five millimeters in diameter, mingled with lustrous angular black grains which were seen under the microscope to be cubes with striated faces, cubes penetrating each other and aggregations of cubes. Combinations of cubes with octahedra and instances of the pentagonal dodecahedron were also observed. These forms, characteristic of pyrites, were also seen in the fine sand obtained as a residue on elutriating the same soil. As these crystals dissolved in hydrochloric acid, giving a strong iron solution, they were regarded as pseudomorphs of iron oxid after pyrites. The yellowish grains on treatment with acid left a grayish residue which contained some grains of quartz, but was not wholly quartz. The lighter portion of the soil, over ninety-nine per cent., which floated in the Thoulet's solution of 2.8 was next examined. It was colored red by the iron oxide which coated and adhered to the other minerals. It contained all the quartz, the feldspars if present, and the other minerals whose specific gravity is less than 2.8. It was examined by the microscope and found to consist largely of irregular grains of a mineral which acted

on polarized light, obscured somewhat by the iron oxid, and which was apparently quartz; and another mineral which was yellowish-brown in color and seemed to be dull and not transparent. Besides there was a large quantity of indistinguishable amorphous material. To clean these minerals the material was treated with hydrochloric acid to remove the iron oxid and other matter soluble in acid, when the quartz grains appeared transparent and gave interference colors in polarized light. But mingled with these were grains of the other mineral which now appeared grayish, dull, and without action on polarized light. The character of this mineral substance could only be determined by chemical analysis

301. Harada's Apparatus.—It is commonly held by analysts that in the subsidence of small particles it is advisable that the containing vessels have parallel sides, yet in the method just given, and in those about to be described, valuable results are obtained in a funnel or pear-shaped holder.

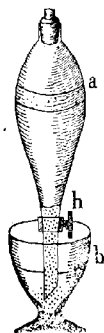


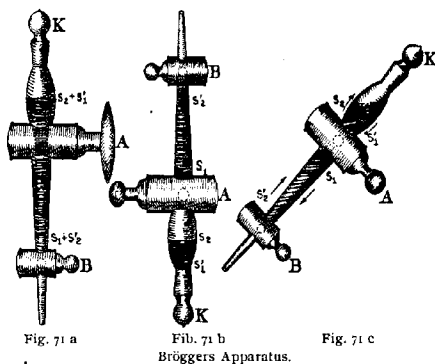
Fig. 70. Harada's Apparatus.

In the apparatus of Harada,¹⁶ which is highly praised by many analysts on account of its simplicity and effectiveness, Fig. 70, the separating vessel *a* is made of thick glass furnished with a glass stopper above and a glass stop-cock *h* below. The separating liquid and silt are placed in the pear-shaped vessel *a*, the stopper inserted, and the whole well-shaken. As soon as a ring

¹⁶ Rosenbusch, *Mikroskopische Physiographie* : 241.

of clear liquid is seen between the sinking and floating silt, the lower end of the apparatus is brought near the bottom of a conical glass *b*, the cock *h* opened and the heavy silt allowed to fall out. Very little of the liquor will flow out because of the air pressure. Should an air bubble enter the apparatus and be held at the stop-cock, it should be made to ascend by gently tapping. When all the heavy silt has passed into the conical glass, the cock *h* is closed and some water poured over the solution and silt in *b*. The separatory apparatus is now raised until the beveled end of it is in the water layer, when the water at once rises to *h* and thus washes all the silt particles adhering to the glass into *b*. The liquid in *a* may then be diluted by inverting the apparatus, adding the required amount of water through *h*, again shaken after closing *h*, and another separation secured as before.

This apparatus is somewhat easier to manipulate than Thoulet's but does not admit of the same exact quantitative dilution of the separating liquid.



302. Apparatus of Brögger.—All silt separations in narrow tubes are open to the objection of permitting more or less flocculation. Some of the lighter particles are thus carried down by the heavier, and, on the other hand, some of the heavier float with the lighter. This disturbing action Brögger¹⁷ seeks to avoid by the

¹⁷ Geologiska Föreningens i Stockholm Förhandlingar, 1884. 7 : 417.

following device, shown in different positions in Fig. 71, a, b, c. The length of the apparatus is forty-six centimeters, and its greatest diameter 3.5 centimeters. The opening in the large stop-cock A is the same diameter as that of the apparatus at that point. The cubical content of the apparatus with A open and B closed is about seventy-five cubic centimeters. In conducting the separation the cock B is closed, the separating liquid and silt introduced, A being open, the stopper K inserted and the whole well-shaken. In the first separation, the silt S_1 , lying over B is contaminated with some of the lighter particles S'_2 , while the lighter particles above A, S_2 , are mixed with some of the heavier particles, S'_1 . After closing A the apparatus is again well-shaken and inverted as in Fig. 71 b. The two parts of the silt will now undergo another separation as indicated. The apparatus is now carefully inclined as in c, when the various grades of silt will flow in the directions indicated by the arrows, but without mixing, passing each other on opposite sides of the apparatus. When the movement is complete, A is carefully opened, the apparatus still

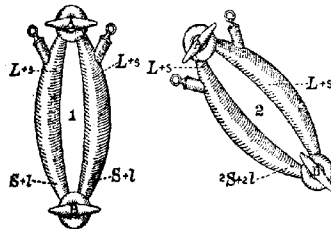


Fig. 72. Apparatus of Wulffing.

being held as in c, and the light silt formerly between A and B will flow above A, while the heavy silt above A will flow down and join the silt collected over B. This operation may be repeated until a perfect separation is affected. Finally B is opened and the heavy silt collected in a beaker, and the lighter silt then removed from the upper part of the apparatus.

303. Method of Wulffing.—A somewhat more convenient method of purifying the silt segregates and freeing them of mechanically occluded particles of differing specific gravities has been

proposed by Wülfing.¹⁸ An elliptical ring of heavy glass tubing carries glass stop-cocks A and B, Fig. 72, at the two extremities of the ellipse, each arm of which is provided with a lateral glass-stoppered neck. The perforation in the stop-cocks has the same diameter as the ends of the ellipse. The apparatus has an interior content of about forty cubic centimeters. Thirty cubic centimeters of the separating fluid are introduced through one of the lateral apertures and brought to the same height in the two arms by opening the cock B. The silt is then introduced in equal quantities into each of the arms. The stoppers having been inserted, the whole is well-shaken. At the beginning of the separation, the apparatus being held in a vertical position 1 the lighter soil above and the heavier soil below are somewhat mixed by reason of flocculation and mechanical entanglement. At this point B is opened and the apparatus placed in the inclined position 2. The heavier particles $S + l$, on the right arm 1 are thus united with the same class of particles in the left arm 2 making $2S + 2l$. This operation is hastened by opening A and allowing the higher column of liquid in the right arm to pass into the left. The liquid in the left arm is allowed to rise to A. After all of $S + l$ in the right arm has passed into the left, B is closed, the apparatus then placed back in position 1 and inclined in the opposite direction until $L + s$ in the top of the left arm has been transferred to the $L + s$ in the top of the right, and the same quantity of liquid is found in each arm. The operation is then repeated and this continued until all $S + s$ is found in the bottom of the left arm and all $L + l$ in the top of the right arm.

Somewhat different forms of apparatus for conducting separations of this kind have been suggested by Laspeyres.¹⁹

304. Separation with a Magnet.—Particles of magnetic iron oxid are easily separated from the fine soil particles by means of a magnet. A strong bar or horseshoe magnet may be used. Electro-magnets are rarely necessary except for the separation of particles of feeble magnetic power. Particles of iron which may be found might owe their origin to the mortars in which the soil had

¹⁸ Rosenbusch, *Mikroskopische Physiographie* : 243.

¹⁹ *Chemisches Centralblatt*, 1896, 2 : 817.

been pulverized, or they might come from a recently crushed meteorite or magnetic ore. Some minerals, as limonite, after ignition are attracted by the magnet and it is advisable to subject a part of the sample to this treatment. The best method of separation consists in spreading the particles evenly on paper and gradually bringing the magnetic particles to one side by moving the magnet underneath.

305. Abundance of Mineral Compounds in the Soil.—The detection of mineral fragments in the soil by means of separation of the soil particles into groups by size and by specific gravity renders it more easy to distinguish the kinds of mineral fragments present by microscopic and microchemical means. Thus the nature of these fragments is revealed and additional knowledge of soil in respect of its original constitution obtained.

Delage and Lagatu have pointed out the very numerous kinds of minerals in soils.²⁰

Carbonate of lime in two forms, hyalin quartz and one other variety, schists, muscovite and biotite micas, sericite, orthoclase and oligoclase feldspar, pyroxene, augite, amphibole, sphene, zircon, apatite, chlorite, serpentine, limonite and oligist iron minerals were found in a single sample of soil.

306. Color and Transparency.—But little can be learned from the color and transparency of the smallest silt particles, but these properties in the larger grains have considerable diagnostic value. Many minerals of distinct color appear wholly colorless in petrographic sections or in silt particles, as for instance, highly-colored quartz. On the other hand, even the smallest particle of chlorite will show its distinctive tint. The colors in some minerals are due to occluded matter not essential to their structure, and these foreign bodies would naturally escape when the crystal mass is reduced to an almost impalpable powder.

307. Value of Silt Analyses.—As in the case of chemical analyses a silt analysis of a soil which is not typical or representative has little value. On the other hand, a systematic separation of soils into classes of particles can not fail to reveal a definite correspondence of mechanical composition to physical soil properties.

²⁰ Comptes rendus, 1904, 139 : 1233.

The production of a crop is the result of certain environments, chief among which are temperature, moisture, and plant food. In a given soil the temperature is markedly affected by its physical state. It has been demonstrated in previous paragraphs that the circulation of moisture in the soil and its capacity to be held therein are chiefly functions of the state of aggregation of the soil itself. The availability of plant food in a soil is not measured by its quantity alone, but also by its state of subdivision. It is not therefore a matter of surprise that the fertility of a soil is found, *cæteris paribus*, to be commensurate to a certain limit with the percentage of fine silt and clay which it contains. It is true that two soils quite different in fertility, may have approximately the same silt percentages, but in such a case it is demonstrable that even in the poorer soil the measure of fertility is largely the percentage of fine particles in connection with its actual content of plant food. Many soils may have large quantities of plant food, but these stores, owing to certain physical conditions, are not accessible to the rootlets of plants. An illustration of this is seen in the use of concentrated fertilizers. It might seem absurd to suppose that the addition of 100 pounds of sodium nitrate would prove useful to a plat containing already a much larger quantity of nitrogen; but the nitrogen of the nitrate is at once available and its beneficial influences are easily seen.

The full value of silt analysis will only be appreciated when many typical soils from widely separated areas are carefully studied in respect of their chemical and physical constitution and the character of the crops which they produce.

PART FIFTH

ESTIMATION OF GASES HELD IN SOILS.

308. Relation of Soil Composition to Gases.—The power of a soil for occluding gases rests primarily on its composition as determined by silt analysis. The discussion of this part of the subject is so nearly related to that of the physical properties of the soil that it might properly have been included in that part of the work. Since, however, we deal in this part more with the determination of the gas constituents of the soil, it was deemed preferable to place it after the silt analysis and as introductory to the general estimation of the chemical constituents of the soil.

309. Occurrence of Carbon Dioxid.—*Aside from the elements of the atmosphere by far the most important gaseous constituent of the atmosphere is carbon dioxid. The amount of organic matter in the soil is not necessarily an indication of the quantity of carbon dioxid when the organic matter is in excess. The percentage of carbon dioxid is only proportional to the amount of organic matter when this is in small quantities. Large quantities of organic matter do increase the amount of carbon dioxid, but the increase is not a proportional one, since a larger quantity of this gas in the air of a soil reduces the activity of the organisms which produce oxidation. Water and temperature have a great influence on the oxidation of the organic matter, which depends chiefly upon the activity of ferments of various kinds. The amount of free gas in the soil affords no certain indication either of the intensity of the action of oxidation or of the amount of organic matter. The carbon dioxid found in the soil may have its origin partly in the rain water which dissolves it from the atmosphere in subterranean sources or more frequently from the decay of the organic matter in the soil naturally or that which is added thereto in the application of organic fertilizers.*

310. Absorption of Aqueous Vapor.—The power of a soil to resist drought depends largely upon its coefficient of absorption for

aqueous vapor. In general, clay soils are more absorbent than sandy ones, yet there is no direct connection between the amount of clay present and the absorbent power of the soil. Evidently the hygroscopic coefficient is largely controlled by the presence with the clay of the powdery ingredients which determine its looseness of texture, and it is found that the finer silts possess considerable absorbing power. The movement of aqueous vapor from the air to the soil or *vice versa* depends on the conditions of equilibrium which may obtain. Whenever these are such that moisture is attracted one way or the other, a movement will always be started towards the reestablishment of equilibrium. It is evident that the relation of a soil to the air in so far as its ability to attract hygroscopic moisture is concerned depends largely on the size and chemical structure of its particles.

311. Methods of Study.—The study of the deportment of a soil with vapors or gases may be divided into two general classes. The first depends on the subjection of a sample of soil to the saturating influence of a given vapor or gas and measuring the amount thereof absorbed, either directly by increase of weight, or by the diminution in the amount of gas originally supplied. The maximum absorbent capacity of a soil under given conditions for a gas or vapor is in this way determined.

In the second class the determination consists in accurately estimating the amount of gas which is absorbed by a soil in natural conditions or *in situ*, thus giving the natural percentages of the gaseous constituents of the soil.

In the first case in general, the principle of the method depends upon the exposure of the soil for a given time under given conditions, to an atmosphere of the gas to be absorbed. The principle of the second class of determinations depends upon the extraction, usually by means of suction, from a given mass of soil of the gaseous matters therein contained. The general details of the methods of procedure for the first class are found in the following directions for manipulation:

312. Determination of the Maximum Hygroscopic Coefficient.—The fine earth, in Hilgard's method, is exposed to an atmosphere saturated with moisture for about 12 hours at the ordinary

temperature (60° F.) of the cellar in which the box should be kept. The soil is sifted in a layer of about one millimeter thickness upon glazed paper, on a wooden table, and placed in a small water-tight covered box, twelve by nine by eight inches, in which there is about an inch of water; the interior sides and cover of the box should be lined with blotting paper, kept saturated with water, to insure the saturation of the air.

Air-dried soil yields results varying from day to day to the extent of as much as thirty to fifty per cent, nor have we any corrective formula that would reduce such observations to absolute measure. Knop's law, that the absorption varies directly as the temperature, while applicable to low percentages of saturation, is wide of the truth when saturation is approached. The ordinary temperature of cellars will serve well in these determinations without material correction.

After from eight to twelve hours the earth is transferred as quickly as possible, in the cellar, to a weighed drying tube and weighed. The tube is then placed in a paraffin bath; the temperature gradually raised to 200° and kept there from 20 to 30 minutes, a current of dry air passing continually through the tube. It is then weighed again and the loss in weight gives the weight of hygroscopic moisture from saturated air.

The reason for adopting 200° as the temperature for drying instead of 100° is that water will continue to come off from most soils at the latter temperature for an indefinite time, a week or more, before an approach to constancy of weight is attained; and that up to 200° only an arbitrary limit can be assigned for the expulsion of hygroscopic moisture. Moreover, the great majority of soils, especially those poor in humus, will reabsorb moisture from a saturated atmosphere to the full extent of that driven off at 200°.

313. Estimation of the Absorption Power of Soils for Aqueous Vapors.²¹—*Method A.*—The fine earth, from ten to 20 grams, is spread out on a surface of about 25 square centimeters, and left for several days. The temperature of the air and the loss of

²¹ König, *Untersuchung landwirtschaftlich und gewerblich wichtiger Stoffe*, 2nd edition, 1898 : 61.

weight are determined from time to time. This evaporation is continued until the weight remains practically constant. Afterwards by drying the sample at 100° the amount of hygroscopic moisture is determined. A similar result can be reached if the sample is first dried at 100° , or over sulfuric acid at ordinary temperatures, and then the increase in weight observed which the sample acquires on being exposed for several days to the atmosphere under ordinary conditions. Soils with about the same content of humus show variations in the power to absorb aqueous vapors which are almost proportional to the amount of clay which they contain. With the increase of humus substance, the power of the soil for absorbing moisture is increased, so that a sandy soil which is rich in humus often will retain as much moisture in an air-dried state as a clay soil which is poor in humus. If the experiment is carried on by drying over sulfuric acid instead of at 100° , the sample should be left from four to seven days in order that a constant weight may be reached. Even after this time the loss in weight is generally from 0.2 to 1.5 per cent less than when the sample is dried at 100° .

Method B.—In order to determine the amount of aqueous vapor which a soil will absorb in an atmosphere saturated with the vapor the following method is used:

The sample of air-dried soil in a flat dish of given surface *viz.*, about 20 grams of soil to 25 square centimeters surface, is placed in a vessel over water without contact with the water, and the whole of the apparatus is covered with a glass bell-jar. The sample is weighed at intervals of from six or eight hours until no appreciable increase of weight is observed. An empty vessel of the same size and character as that containing the soil is kept under the bell-jar, also in the same conditions, so that any increase in weight by the deposition of moisture on this vessel may be determined. This increase in weight is to be deducted from the total increase in weight of the vessel and the soil. Sandy and loamy soils become saturated in this manner in the course of the first 24 hours and remain after that unchanged in weight. Very clayey soils, and also those which are very rich in humus, require a much longer time, three or four days even. In this case it is better to

take a smaller sample of the soil; *viz.*, ten grams. The temperature of the air within the glass vessel, of course, must be taken into consideration.

Method C.—The same flat dish and the same quantity of soil as in the other methods are used in this determination. The sample is left out over night where it can be fully saturated with dew. The amount of dew which appears on the bushes should be noted and also the temperature of the air and the percentage of clouds in the sky. An experiment should also be made on spots of earth which are entirely free from vegetation in order that the difference in the amount of water absorbed in places practically devoid of dew and in places where the dew is abundant may be observed.

Method D.—Deeper flat dishes are used for this determination so that the depth of soil contained in them shall be from one to three, or even six centimeters. The sample of soil is completely air-dried and in a state of fine subdivision. The vessels containing the soil are placed in a locality saturated with aqueous vapor or in the open air during the night where they are subjected to the influence of the cooling of the atmosphere and the deposition of dew. Note is made of the different amounts of moisture absorbed by the layers of earth of different thicknesses in a given time. Observation is also made of the depth to which the moisture sinks in the sample of soil under consideration.

314. Estimation of the Absorption Power of the Soil for Oxygen and Atmospheric Air.²²—From 50 to 100 grams of air-dried soil are placed in a glass vessel of about 500 cubic centimeters capacity, and the flask closed with a stopper after the addition of enough water to make the percentage of moisture in the soil about 20. After from eight to fourteen days the air contained in the vessel is analyzed for oxygen, nitrogen, and carbon dioxide, with special reference to the determination of how much oxygen has disappeared and how much the carbon dioxide has been increased. As an alternative method, 25 grams of the soil are moistened with tolerably concentrated potash lye in a small glass vessel, which is itself joined with air-tight connections to an

²² König, *Untersuchung landwirtschaftlich und gewerblich wichtiger Stoffe*, 2nd edition : 1898 : 63.

azotometer in which a known volume of air is confined by quick-silver. The glass vessel is frequently shaken during the progress of the experiment. From the diminution of the volume of air in the apparatus after from one to four days the quantity of oxygen absorbed is approximately calculated.

315. General Method of Determining Absorption.—A convenient method is as follows:²³ The soil, in a state of fine powder, is dried at from 100° to 105° to a constant weight. It is then placed in an absorption tube of the following construction:

The absorption tube consists of a U-shaped wide glass tube, both ends of which are supplied with small glass tubes sealed upon the end of the U-tube, and these are furnished with tightly-ground glass stop-cocks. Above these stop-cocks these small tubes are bent in opposite directions at right angles. On the bend of the U is sealed another tube which is furnished with a ground glass stopper. Through this opening the U-tube can be filled with the sample of soil. When the tube is filled, the glass stopper inserted, and the two stop-cocks on the small tubes closed, the contents of the tube are completely excluded from the external atmosphere. Many of these tubes can be used at once so as to hasten the progress of the work.

The tubes after filling are placed in a drying oven with the stop-cocks open. The stop-cocks are closed before the tubes are removed, placed in a desiccator for cooling preparatory to weighing. The weighed tubes are held in a tin box which can be placed in a water-bath which is kept at a given temperature by means of a thermostat. The top of the tin box is hinged and made of a thick non-conducting material so as to prevent any rapid change of temperature within. On the inner side of the box a small thin-walled glass tube is carried around four times. One end of this tube passes through an opening in the side of the box by means of which it can be connected with the gas apparatus outside. The other end of it is connected directly with the absorption tubes.

The absorption tubes are so connected among themselves that when ammonia or carbon dioxide is employed the gas passes

²³ von Dobeneck, *Forschungen auf dem Gebiete der Agrikulturphysik*, 1892, 15 : 163, et seq.

through one of the tubes before it can reach the next, and so on. For experiments with water gas, however, that is, air charged with aqueous vapor, the arrangement must be different. While in the case of ammonia and carbon dioxide the composition of the gas is not changed by passing through the samples of soil, the case is quite different when air charged with aqueous vapor passes through. In the latter case the amount of aqueous vapor in the air would be notably lessened in passing from sample to sample on account of the retention of a part of the aqueous vapor by the soil. In this case, therefore, the saturated air, after it has passed through the glass tube around the inside of the box in order to reach the proper temperature, is conducted into a receptacle of glass which has a number of connections equal to the number of absorption tubes so that the saturated air can pass directly into each one of them.

The gases which are to be used for the experiments are prepared in proper apparatus and are forced through the samples of soil, either by pressure as in the case of ammonia or carbon dioxide, or by means of aspirators as in the case of air saturated with aqueous vapor.

The carbon dioxide employed is purified by passing over sodium carbonate and calcium chloride.

The ammonia is prepared by the action of finely powdered lime on ammonium chloride, and is dried by passing over lime and sticks of potassium hydroxide.

The air which is to be saturated with aqueous vapor, in order to purify it from dust, carbon dioxide, and ammonia, is passed through two flasks in which are contained respectively, dilute sulfuric acid and potash lye. It is afterwards thoroughly saturated with aqueous vapor at the temperature desired.

Various kinds of soil material may be employed as follows:

(1) Pure quartz sand.—Freed from all fine particles by subjection to silt analysis, afterwards boiled with hydrochloric acid and washed with water to free it from all clayey materials. The sand prepared in this way is passed through different sieves in order to prepare it in different states of fineness.

(2) Quartz powder.—Prepared from pure quartz crystals by grinding.

(3) Kaolin.—Material such as is used in the manufacture of the finest porcelain which, after being freed of all foreign matter, is rubbed to a fine powder in a porcelain mortar.

(4) Humus.—Washed with ether and alcohol, boiled with hydrochloric acid, washed, dried, and reduced to a state of fine powder.

(5) Iron oxid.

(6) Calcium carbonate.—Precipitated, washed and dried.

(7) Soil mixtures.—Prepared artificially by mixing the kaolin, quartz, and humus, above mentioned.

The quantity of gas absorbed by each of these materials is determined by filling the tubes, as above mentioned, with the dried material. The content of each tube is previously determined by filling with mercury and weighing. Having determined the weight of the substance after the expulsion or calculation of the volume of the air contained within its pores, it is treated with the gas in the apparatus described above and weighed from time to time until no further increase of weight takes place.

The method of calculating the results is shown in the following scheme:

Let

P' = weight of the empty tube filled with air at 100° .

V = content of the absorption tube.

pl = weight of the air in the tube ($pl = V \times$ specific gravity of the air at 100°).

pt' = weight of the tube ($pt' = P' - pl$).

P^2 (second weighing) = weight of the tube filled with the substance with the included air at 100° .

v^s = volume of the substance calculated according to the formula

$$v^s = \frac{P^2 - P'}{s^s - \text{specific gravity of the air}}$$

s^s = specific gravity of the substance.

vl = volume of the air in the flask filled with the substance ($vl = V - v^s$).

pl' (weight of this included air) = $vl \times$ specific gravity.

p^s = weight of the substance ($p^s = p^3 - pt' - pl$).

P^3 = weight of the apparatus at the end of the experiment.

sg = specific gravity of the gas employed for saturation.

pg (weight of the gas remaining over the substance) = $vl \times sg$.

pa (weight of the absorbed gas) = $P^3 - pt' - p^s - pg$.

Then if p^s gram of substance absorbs pa gram of the gas, 100 grams of substance would absorb $\frac{100 \times pa}{p^s}$ grams.

The specific gravities of the gases employed are calculated from the tables given by Landolt and Börnstein in "Physical and Chemical Tables," page 5.

The specific gravity of the quartz sand employed was 2.639; of the quartz powder, 2.622; of the kaolin, 2.503; of the humus, 1.462; of the iron hydroxid, 3.728; and of the calcium carbonate, 2.678.

One liter of ammonia, at a pressure of 760 millimeters of mercury and a temperature of 0° , weighs 0.7616 gram; one liter of carbon dioxid, 1.9781 grams; one liter of aqueous vapor, 0.8064 gram and one liter of dried-air, 1.2931 grams.

At a pressure of 720 millimeters, and at 20° temperature, a liter of air saturated with aqueous vapor at 0° weighs 1.1383 grams; saturated at 8.6° , 1.1362 grams; saturated at 10° , 1.1358 grams; saturated at 14° , 1.1340 grams; saturated at 18.2° , 1.1330 grams; saturated at 20° , 1.1321 grams; saturated at 30° , 1.1313 grams.

The general results of the experiments are as follows:

ABSORPTION AT 0° .

	Aqueous vapor from saturated air.		Ammonia.		Carbon dioxid.	
	Grams.	Cubic centimeters. ¹	Grams.	Cubic centimeters. ¹	Grams.	Cubic centimeters. ¹
100 grams quartz....	0.159	197	0.107	145	0.023	12
100 " kaolin....	2.558	3,172	0.721	947	0.329	166
100 " humus...	15.904	19,722	18.452	24,228	2.501	1,263
100 " $Fe_2(OH)_6$	15.512	19,236	4.004	5,275	6.975	3,526
100 " $CaCO_3$	0.224	278	0.256	320	0.028	14

¹ Reduced to 0° and 760 millimeters pressure mercury.

The foregoing methods will suffice to show the procedures to be

followed in estimating the maximum amount of any common gas or vapor a given quantity of soil may be made to absorb. We pass next to consider the quantities of gases or vapor soils *in situ* may hold.

316. Method of Boussingault.²⁴—This method is the oldest and most simple procedure for estimating the nature of the gases held in a soil *in situ*.

For the purpose of collecting the sample of gas from the soil a hole from 30 to 40 centimeters in depth, is dug, and a tube placed in it in a vertical position, having on its lower extremity a bulb perforated with fine holes. The hole is filled and the earth closely packed around the tube which is left for 24 hours. At the end of that time the tube is slowly aspirated until a volume of gas approaching from five to ten liters is obtained.

Estimation of Carbon Dioxid.—The carbon dioxid in the sample of gas is estimated by allowing it to bubble through a solution of barium hydroxid.

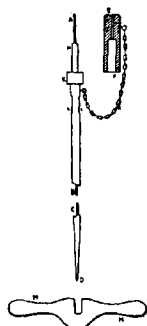


Fig. 73. Schloesing's Soil-tube for Collecting Gases.

Estimation of the Oxygen.—The oxygen is estimated in a separate sample of the gas by means of potassium pyrogallate.

The chief objection to this simple process is the uncertainty of being able to obtain an average sample of the occluded gas. In digging the hole and refilling, there must evidently be a considerable disturbance of the original distribution of the gas or vapor.

²⁴ Encyclopédie chimique, 4 : 199.

No greater detail concerning these methods of the direct aspiration of the air is considered necessary inasmuch as the methods about to be described, while more elaborate, are superior in accuracy to the older methods mentioned. In general, in these experiments, it is deemed sufficient to determine the carbon dioxide only.

317. Method of Schloesing.—The apparatus used by Schlösing²³ in the collection of the soil gases consists of a steel tube (Fig. 73) a little over one meter in length, ten millimeters in external diameter, and one and one-half to two millimeters in internal diameter. The end which penetrates the soil is made slightly conical for a distance of from 25 to 30 centimeters. By reason of the shape of the tube, when it is driven into the soil all connection between the orifice in the point of the tube and the external air is prevented. The obstruction of the internal canal of the tube is prevented by introducing a thread of steel which penetrates the whole length of the tube. This thread, represented by A, B, C, D, is flush with the interior extremity of the tube at D. It extends for about three centimeters above the upper end of the tube in order to be easily handled when it is to be removed.

For the purpose of driving the tube into the soil its upper part is covered with a cylindrical piece of steel, EF, in the interior of which are freely engaged H and A. This head piece rests upon a ring of steel, K. This ring is fastened solidly into the tube. On striking the piece EF the tube and the steel wire in the center are driven together into the soil. The tube is flattened at L and L' in order to be embraced by the key MM, the employment of which is necessary in order to revolve the tube around its axis when it is being driven into the soil. When the tube has been driven to the depth desired, the steel wire is withdrawn and it is immediately connected at H with the rubber tube N (Fig. 74) belonging to the system PQT and furnished with a pinch-cock X. The system PQT comprises the following elements: PQT made of a capillary glass tube in the form of a T. The lower end of the tube P is closed by the larger glass tube O, sealing the end of P with a little mercury. O is held to P by the cork S, which is attached firmly enough to prevent O from dropping off, but is furnished

²³ *Annales de Chimie et de Physique*, 1891, [6], 23 : 362, et seq.

with a canal in order to allow the air to flow in or out freely. This system is connected with the system UV by the rubber connection T. U is a glass vessel having the constrictions as indicated

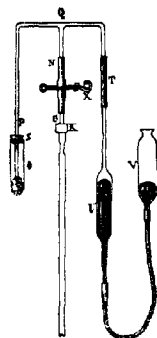


Fig. 74. Schloesing's Apparatus for Collecting Gases from Soil.

in its stem above and below the bulb. V is a glass vessel of convenient size connected with U by the rubber tubing as indicated. The capacity of the cylindrical portion of U should be from 15 to 18 cubic centimeters.

To get a sample of soil gas, F is lifted above U. The air is driven from U and escapes through O, which acts as a true valve. When the mercury has completely filled U the pinch-cock X is opened and V depressed gradually. The gas coming from the soil is thus collected in U. A few cubic centimeters of the soil gas are collected in this way, the pinch-cock X is again closed and V is raised in order to drive the whole of the contents of U again through O. In this way the whole of the air which the capillary vessel originally contained is removed and all parts of it remain filled with soil gas. Two or three operations, using from five to ten centimeters of soil gas in all, will be sufficient to completely free the apparatus from its original content of air. U is then entirely filled by depressing V, and it is then hermetically sealed at the two constricted points by means of an alcohol lamp. The sealed tube can then be transported to the laboratory and its contents subjected to eudiometric analysis.

Without displacing the tube from the soil, several samples of gas can be taken from the same spot. A sufficient number of the bulbs U should be at hand to hold the required number of samples. Instead of submitting the sample to eudiometric analysis it is usually sufficient to determine the quantity of carbon dioxid which it contains, inasmuch as numerous experiments have shown that in 100 parts of soil gas the oxygen and carbon dioxid together constitute 21 parts. No appreciable trace of marsh gas, or other combustible gas, has yet been detected in ordinary arable soils. These gases have only been found in special soils from marshes, in the neighborhood of gas wells, etc., and not in arable soils.

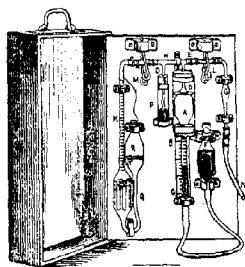


Fig. 75. Schlösing's Apparatus for Determination of Carbon Dioxid.

318. Apparatus for Estimating the Carbon Dioxid.—The apparatus used for determining the carbon dioxid in Schlösing's work consists of the apparatus shown in Fig. 75. A represents a glass vessel surrounded by a jacket of glass, full of water, and sealed on its lower part to the tube BC of about six millimeters internal diameter. On its upper part it is sealed to the capillary tube D. The tube BC is graduated from C in hundredths of the volume of DAC, which volume is about 12 cubic centimeters. On its lower part it is connected by a rubber tube with a reservoir F which is capable of being raised or lowered. GHK are capillary tubes connected together by the rubber tubes L and M, which are furnished with pinch-cocks. The tube G is connected to a vacuum by the rubber tube N. The rubber tube should be of very small

internal diameter and from 40 to 50 centimeters in length. To the tube H are sealed, at right angles, the branch D and another branch O. This last dips into a little mercury which the tube P contains. It serves as a valve, permitting the exit of the gases but not their entrance. The tube K carries some lines engraved on its inferior part and is sealed to the system of the two bulbs Q and R. The bulb Q contains a concentrated solution of potash. It carries a number of pieces of glass tubing for the purpose of increasing the surface of the potash solution.

All the parts of the apparatus are fixed upon a rectangular board, 19 centimeters broad by 20 centimeters long. This forms one of the faces of a wooden box to which it is hinged and which serves for the transportation of the apparatus in a vertical position. The graduation of the tube BC is recorded behind this tube upon a card fixed upon the board. By means of these two graduations, the height of the mercury in the tube BC is most easily read, even when the tube is not perfectly vertical. Each one of the pinch-cocks L and M, on its upper part is fixed in a sort of guard which prevents it from being displaced laterally during the processes of the manipulation, thus avoiding all danger of breakage.

After the operation is finished a little air is sent into Q in such a manner as to sensibly lower the level of the solution of potash, and the upper extremity of R is closed with a rubber stopper. Afterwards, the apparatus can be transported without any danger of the potash becoming engaged in the tube K and reaching the measuring tank A.

To proceed to the analysis, a stake is driven into the soil to which all of the apparatus can be fixed. At the side of the stake the apparatus for taking the sample, already described, is driven into the soil and this apparatus is connected by the tube N with the apparatus for determining the carbon dioxide. The pinch-cocks L and M being closed, F is lifted until the mercury which runs from it fills A and approaches D. During this time the air which the apparatus contains has been driven out through O. The tube NGD is freed from air by opening the pinch-cock L, lowering F and drawing into A the gas coming from the soil; after-

ward closing L, and driving out the gas through O. After two or three rinsings of this kind, which employ altogether only ten to 12 cubic centimeters, the gas which is to be analyzed is sucked into A. For this purpose F is lowered until the mercury in the tube BC is very near C. The pinch-cock L is closed and M opened. The reservoir F is displaced little by little by pressing lightly against the rectangular board in order to give it greater firmness in such a way as to fix the level of the mercury exactly at C, and the line is noticed where the solution of potash in K stands. The gas contained in the apparatus is under a pressure, the difference of which from the external pressure is represented by the column of the potash solution between the mark just noticed and the level of the same solution in the bulb R. In order to absorb the carbon dioxid, F is lifted until the mercury stands between D and E. The gas thus passes from A into Q. It gives up immediately its carbon dioxid to the potash solution. It is then made to come again into A, and afterward a second time into Q, in order to free it from the last trace of dioxid. Finally it is made to return to A and F is kept at such a height that the potash solution maintains in the tube K the same level as at the commencement of the operation. The gas is then at the same pressure to which it was subjected before absorption. The level of the mercury is then read on BC. At the time the apparatus is used, the measuring tube A should be slightly moist. If it is not so, a small quantity of water should be introduced which is afterward rejected, but which leaves a sufficient quantity of moisture upon the internal walls of A. In this way the gas will always, before or after absorption of carbon dioxid, be saturated with vapor of water, and the figure read in the last place upon the tube BC represents the percentage of carbon dioxid in 100 parts of the gas extracted from the soil supposed to be saturated with vapor at the temperature of the experiment.

During the course of the analysis, the temperature of the measuring flask, which is almost entirely surrounded with water, does not vary sensibly, but in a series of experiments which are executed at different times, the temperature of the measuring apparatus, which is that of the ambient air, may change much. It may oscillate between 10° and 25°, and exceptionally between 0°

and 30° , whence there are notable variations in the tension of the vapor of the gas measured. If it should be desired to calculate to 100 parts of dry gas the observations made at 30° upon 100 parts of saturated gas, it would be necessary to increase the percentage of carbon dioxide by about $\frac{1}{25}$ of its value. It is noticed that with the apparatus described above, the gas upon which the estimation is really conducted comprises not only that which the measuring apparatus contains from E to C before the absorption of the carbon dioxide, but also the small quantity which remains in the capillary tube KME at the moment when closing the pinch-cock M, after the second rinsing, the gas from the soil is aspired into EAC. On the other hand, there is left in the same tube KME when the final reading is made, some gas which belongs to that which has been measured at the end. These two small gaseous portions which we consider in the tube KME to be sensibly equal, do not contain any carbon dioxide and may be left out of consideration. That is why the volume of the measuring apparatus is limited to E and the graduation of the tube BC is in hundredths of the volume comprised from E to C. In reality the two portions are not absolutely equal because the two successive levels of the potash solution, which limit them in the tube K, are not absolutely identical. These two levels can differ in such a manner as to correspond to a volume of about $\frac{1}{1000}$ of the measuring apparatus. Thus the estimation is really made upon a volume of gas which may be greater or less by $\frac{1}{1000}$ than the volume of EAC; whence there might result an error of $\frac{1}{1000}$ in the estimation of the carbon dioxide, an error which is wholly negligible.

As a result of numerous analyses it is concluded, first, that the oxygen exists normally in the atmosphere of soils in large proportion; second, very probably the gaseous atmosphere of arable soils, to a depth of 60 centimeters, contains scarcely one per cent of carbon dioxide and about 20 per cent of oxygen; third, the highest percentages of carbon dioxide correspond to epochs of highest temperature and periods of greatest calm; fourth, the proportion of carbon dioxide increases ordinarily with the depth at which the samples are taken. This disposition of the carbon dioxide is not surprising, since near the surface the internal atmosphere is almost constantly diluted by external air by virtue of diffusion.

Fifth, from one epoch to another the composition of the atmosphere of the soil can undergo considerable variation.

319. Determination of Diffusion of Carbon Dioxid in Soil.—The method proposed by Hannén²⁸ is a convenient one to use in studying the rate of diffusion of carbon dioxid in soils. A large Woulff's bottle with three necks serves for the reception of the gas. The two smaller outer necks of the bottle carry two glass tubes bent outwards and provided with stop-cocks. One of these passes to near the bottom of the bottle and the other just through the stopper. The middle tubule of the bottle is of a size to give in section an area of about 22 square centimeters. It is made with a heavy rim two centimeters wide and plane ground. This rim carries a plane-ground glass plate with a circular perforation in one-half of it, of the size of the opening in the central tubule of the bottle. A glass cylinder, carrying a fine wire-gauze diaphragm near the lower end, fits with a ground-glass edge air-tight, over this aperture, being held in position by a brass clamp. The ground-glass plate moves air-tight between the cylinder and the bottle, so that the cylinder can be brought into connection with the bottle or cut off therefrom without in any way opening the bottle to the air. The plate and all ground movable surfaces should be well lubricated with vaseline.

The experiment is carried on as follows: The glass cylinder is filled with the soil to be tested, closed above with a rubber stopper carrying a gas tube, and then by moving the perforated glass plate brought into connection with the bottle. The side tube, with short arm inside the bottle, is then closed, and carbon dioxid introduced through the other lateral tube until the gas passing from the tube at the top of the cylinder is pure carbon dioxid.

The lateral tube is then closed and the bottle is placed in a water-bath and kept at a constant temperature of 20°. When the temperature within and without the apparatus is the same the reading of the barometer is made, the stopper removed from the top of the cylinder, and the process of diffusion allowed to begin. After from six to ten hours the glass plate is moved so as

²⁸ *Forschungen auf dem Gebiete der Agrikulturphysik*, 1892, **15** : 8, et seq.

to break the connection between the cylinder and bottle. The carbon dioxide remaining in the bottle is driven out by a stream of dry, pure air. The air is allowed to pass through the apparatus for about ten hours. The carbon dioxide driven out is collected in an absorption apparatus and weighed. The absorption apparatus should consist of a series of Geissler potash absorption bulbs and finally a U form soda-lime tube. In front of the absorption apparatus is placed a drying bulb containing sulfuric acid. Inasmuch as the temperature and pressure can be readily determined, the weight of carbon dioxide obtained is easily calculated to volume.

The weight of 1,000 cubic centimeters of carbon dioxide at 0° and 760 millimeters pressure is 1.96503 grams. Therefore one milligram is equivalent to 0.5089 cubic centimeter of the gas. The volume of the bottle should be carefully determined by calibration with water. The results should be calculated to cubic centimeters per square centimeter of exposed surface in ten hours. The depth of the soil layer is conveniently taken at 20 centimeters.

320. Statement of Results.—

THE SOIL PACKED LOOSELY IN THE DIFFUSION TUBE. DIFFUSION TIME, TEN HOURS.

Diameter of soil particles. mm.	Weight of soil taken. Grams.	Pure carbon dioxide at beginning of experiment. cc.	Carbon dioxide at end of experiment. cc.	Cubic centimeters of carbon dioxide diffused for each square centimeter.
0.01-0.071	520	2549.4	1230.3	59.9
0.071-0.114	550	2545.9	1269.2	58.0
0.114-0.171	590	2556.4	1354.2	54.6
0.171-0.250	620	2538.9	1336.1	54.6
0.250-0.500	660	2532.0	1374.5	52.6
0.500-1.000	680	2528.2	1440.2	49.5
1.000-2.000	690	2496.6	1396.9	50.0
Mixture of the above	720	2514.3	1572.5	42.8

In greater detail the calculation and statement of the results may be illustrated by the following data:

In the first experiment given in the above table the diameter of the soil particles varied from 0.010 to 0.071 millimeter. The weight of soil in the diffusion tube was 520 grams. The volume of gas, at 0° and 760 millimeters, before the diffusion began was 2549.4 cubic centimeters. The volume of carbon dioxide under

standard conditions remaining after ten hours of diffusion was 1230.3 cubic centimeters. This volume is calculated from the weight of carbon dioxid obtained in the potash bulbs, each milligram being equal to 0.5089 cubic centimeter of carbon dioxid. The volume of carbon dioxid diffused is therefore $2549.4 - 1230.3 = 1319.1$ cubic centimeters. The per cent of carbon dioxid diffused is $1319.1 \div 2549.4 = 51.74$. The volume of carbon dioxid diffused for each square centimeter of cross section of the diffusion tube is $1319.1 \div 22 = 59.9$ cubic centimeters.

The carbon dioxid should be passed long enough to secure complete expulsion of the air before the determination is commenced.

321. General Conclusions.—The general results of the experiments with the diffusion apparatus to determine the effect of the physical condition of the soil upon the rate of diffusion are as follows :

1. The diffusion of carbon dioxid through the soil is, at a constant temperature, chiefly dependent upon the pores in the cross section of the column of soil. Therefore, the absolute quantity of the diffused gas is greater the larger the total volume of the pores and *vice versa*.

2. Every diminution of the volume of the pores, whether secured by pressure of the soil or by an increase in the moisture thereof, is followed by a decrease in the volume of diffused gas. The giving up of the carbon dioxid present in the soil atmosphere to the upper atmosphere by the method of diffusion is therefore the less the finer the soil is, the more compressed the soil particles are, and the larger the water content of the sample and *vice versa*.

3. The quantity of diffused carbon dioxid is diminished according to the measure of compression to which the soil is subjected but is not strictly proportional to the height of the soil layer.

4. In soils in which rain water percolates slowly the diffusion of the carbon dioxid on account of this property is depressed to a greater or less extent.

PART SIXTH

THE CHEMICAL ANALYSIS OF SOILS

322. Preliminary Considerations.—The sample of soil intended for chemical analysis should consist of the fine earth which has passed at least a one-millimeter mesh sieve and subsequently been completely air-dried. The time required for the air-drying of a soil varies with the nature of the soil, the temperature and the quantity of aqueous vapor in the air. Sandy soils dry rapidly and those containing large quantities of humus slowly. A high temperature accelerates and a humid atmosphere retards the process. Under the usual conditions and when the soil is exposed in thin layers, the drying should continue for about four days for an ordinary arable soil, and about six days for one very rich in organic matter. With peat and vegetable soils ten or 12 days with frequent stirring, even when in thin layers, are necessary to attain approximately a constant weight.

The soil is conveniently spread on a zinc or other metal sheet of sufficient area so that the layer will be only one or two centimeters in thickness. The weight before and after desiccation will give the percentage of moisture lost on air-drying, which, of course, will depend chiefly on the degree of saturation of the sample when taken and the atmospheric conditions prevailing during drying.

If samples of soil are got in very dry times it is often necessary to moisten them with distilled water in order to prepare them properly for air-drying.

The quantity of hygroscopic water which the sample loses at 100°-105° should be determined, and all subsequent calculations of the percentages of the various constituents be based on the water-free material. When a soil which has been dried at 100°-105° to a constant weight is heated to 140°-150° it loses additional weight not due necessarily to loss of water of constitution. A part of this loss may be due to hygroscopic moisture which is not given off at 100°-105°, and a part may be hydrocarbons, or other easily

volatile or decomposable organic or inorganic bodies. Before estimating the total loss on ignition it is recommended by most chemists to dry at 140° - 150° . The samples of soil, however, intended for chemical examination should never be dried beyond the point which is reached by exposure in thin layers at ordinary room temperatures. The state of aggregation, degree of solubility, and general properties of a soil, may be so changed by absolute desiccation as to render the subsequent results of chemical investigation somewhat misleading. In the methods which follow the actual processes employed have been given, which in some instances transgress the general principle stated above, but in all cases standard and approved methods are given in detail, even if some of their provisions seem unnecessary or imperfect.

323. Order of Examination.—First of all in a chemical study of the soil should be determined, its reaction (with litmus), its water-holding power in the air-dried state (hygroscopicity), its content of combined water (hydrous silicates of alumina), its organic matter (humus and organic nitrogen), its content of carbon dioxid (carbonates of the alkaline earths), and the part of it soluble in strong acids. A determination of these values gives the analyst a general view of the type of soil with which he is engaged, and leads him to adopt such a method of more extended analysis as the circumstances of the case may demand.

For this reason those operations which relate to the above determinations are placed first in the processes to be performed, while the estimation of the more particular ingredients of the soil is left for subsequent description.

Next follows a description of the standard methods of estimating the more important elements passing into solution on treatment of a soil sample with an acid. The method of treating the insoluble residue, and the detection and estimation of rare or unimportant soil constituents, closes the analytical study of the soils.

With respect to the determination of nitrogen as nitric or nitrous acid in the soil and drainage waters, it has been thought proper to collect all standard methods relating particularly thereto into one group, and since these compounds are more nearly re-

lated to fertilizing materials they will only be noticed briefly in this volume and be given in full in the next.

The question of the practical utility of chemical soil analysis is one which has been the subject of much discussion. There is, of course, no question of its scientific value in connecting the soil with the rocks whose decay has furnished the principal part of its mass and in disclosing the total quantity of plant foods which it contains. A review of the various opinions entertained on this subject finds no proper place in a work of this character. Unless, however, intelligent soil analysis be productive of some good it would be a thankless task to collect and arrange the details of the processes employed. An accurate determination of the constituents of a soil may not always enable the chemist to recommend a proper course of treatment, but it will help in many ways to develop a rational soil diagnosis which will permit the physician in charge of the case, who last of all is the farmer, to follow a rational treatment which in the end will be productive of good.

The analyst will find in the methods given all that are approved by bodies of official or affiliated chemists, or by individual experience, and among them some method or methods which, it is hoped, will be suited, in the light of our present knowledge, to each case which may arise.

324. Reaction of the Soil.—In soils rich in decaying vegetable matter the excess of acid is often great enough to produce a distinct acid reaction.

On the contrary, in arid regions the accumulation of salts near the surface may produce the opposite effect.

In calcareous soils the excess of carbonate of lime is sufficient to maintain at all times at least a neutral state.

The causes of soil acidity, or rather of that condition of the soil which is corrected by lime, are not well understood.

The reaction of the soil is determined with a large number of indicators among which, for convenience and reliability, sensitive litmus paper, both red and blue, stands in the front rank. A sample of the soil, from 15 to 30 grams, is mixed with water to a paste and allowed to settle. The litmus paper is then dipped into the supernatant liquid. When the soil is very moist the lit-

mus paper is applied directly to its cut surface. Detailed methods of quantitatively determining the acidity of soils are given further on.

325. Determination of Water in Soil.—The following problems are presented:

(a) *The Determination of Water in Fresh Samples taken in Situ*—The content of water in this case varies with the date and amount of rain-fall, the capacity of the soil for holding water, the temperature and degree of saturation of the atmosphere, and many other conditions, all of which should be noted at the time the samples are secured.

(b) *The Determination of Water in Air-Dried Samples.*—In this case the soil is allowed to remain in thin layers, and exposed to the air until it ceases to lose weight. The quantity of water left is dependent on the capacity of the soil to hold hygroscopic water and to the temperature and degree of saturation of the air.

(c) *The Determination of the Total Water by Ignition.*—This process not only gives the free and hygroscopic moisture, but also combined water present in the hydrous silicates and otherwise. The estimation is complicated by the presence of carbonates and organic matter.

326. Determination of Water in Fresh Samples.—This determination requires that the sample, when taken from the field, should be so secured as to be weighed before any loss of moisture can take place. For this purpose it can be sealed up in tubes or bottles and preserved for examination in the laboratory.

The prime importance of water to plant growth renders of importance those processes which give accurate information respecting the water content of a soil and the relations of the water so contained to the needs of the plant. The actual percentage of water in a soil is always to be correlated with the properties of a soil for holding moisture. A sandy soil for example may furnish a growing plant with the necessary water long after its percentage content of moisture falls below the limit for a clay soil to sustain the same plant.

The samples are secured as described in paragraph 75. The locality and date are written on a label attached to the tube. The

tube holds from 60 to 70 grams of soil, and the moisture determination is made on this in the laboratory in the usual way.

It is desirable to have this sample represent a depth of from six to nine inches, thus rejecting the surface three inches, which are more liable to sudden and accidental changes.

327. Method of Berthelot and Andre.—The estimation of the water according to Berthelot and André²⁷ should be made under three forms; *viz.*,

1. Water eliminated spontaneously at ordinary temperatures.
2. Water eliminated by drying to constant weight at 110°.
3. Water eliminated at a red heat.

The water may be determined directly on a sample weighed at the time of taking and afterwards dried in the open air, and finally, if necessary, in a desiccator. For general purposes a sample of 100 grams, for exact work ten grams is exposed to the air. The dish in which the drying takes place is shallow, and during the time the sample is frequently stirred and thoroughly pulverized with a spatula which is weighed with the dish. The drying in the air is continued several days. The data obtained are not constant since they depend on the temperature and the degree of saturation of the air with aqueous vapor. The variations due to these causes, however, are not very wide. The process may be regarded as practically finished when successive weights sensibly constant are obtained. In this state the soils contain very little water eliminable at 110°. Drying in a desiccator over sulfuric acid presents few advantages over the process just described.

328. Drying in a Desiccator.—The sample dried as indicated above by the method of Berthelot and André is placed in a desiccator over sulfuric acid. It is better to have the sample traversed by a current of perfectly dry air, and in this case it should be placed in a tube, which is closed while weighing, to prevent absorption of moisture. Much time is also required for this operation, and it does not possess the practical value of the method of drying in the free air.

329. Water Set Free at 110°.—This is determined by Berthelot and André on a weight of from five to ten grams of soil. The

²⁷ *Annales de Chimie et de Physique*, 1892, [6], 25 : 292, et seq.

sample which has been employed for the preceding determination may be used. While this is going on in an air-bath heated at 110° , about ten times as much soil should be dried for the same time at the same temperature, and this should be preserved in a well-stoppered flask. All subsequent determinations are to be made with the soil dried at 110° .

The loss of weight in a soil increases with the temperature to which it is exposed. The apparent quantity of water, therefore, determined at 140° or 180° is always greater than that obtained at 110° . But when the temperature exceeds 110° there is danger of decomposing organic bodies with the loss of a part of their constituent elements. Carbon dioxide and ammonia may also be lost, as well as other volatile bodies.

330. Estimation of Water Remaining After Air-Drying.—The sifted sample is placed in quantities of five or ten grams in a flat-bottom dish and dried at 110° to constant weight. Finally the sample is incinerated, thus obtaining the water of constitution along with organic matter and carbon dioxide in carbonates. This treatment not only removes the moisture, but all other matters volatile at that temperature.

Petermann,²⁸ advises drying the sample to constant weight at 150° .

It is further recommended by Petermann to determine total volatile and combustible matters by igniting to incipient redness, allowing to cool, moistening with distilled water, and drying at 150° . In thus expelling both water of constitution and organic matter and restoring the water of constitution by subsequent moistening, it is claimed that a near approach to the real quantity of organic matter is secured. If all the water of constitution is restored this is doubtless true. The possibility of so changing the nature of the colloidal particles by ignition as to prevent them from reabsorbing the original content of water must be taken into consideration. There is little danger of decomposing carbonates by heating to incipient redness for a short time.

The analytical processes followed by the German Agricultural

²⁸ *L'Analyse du Sol*, Brussels, 1891 : 14.

Chemists²⁹ are performed on air-dry soils, except as noted below and the results calculated to the weight of soil dried at 100°. In determining loss on ignition, however, the preliminary drying is made at 140°, with the exception of peaty samples where so high a temperature is not admissible.

The Official Agricultural Chemists³⁰ advise to place five grams of air-dry soil in a flat-bottom and tared platinum dish; heat in an air-bath to 110° for eight hours; cool in a desiccator, and weigh; repeat the heating, cooling, and weighing, at intervals of an hour till constant weight is found, and estimate the hygroscopic moisture by the loss of weight, ascertained rapidly to avoid absorption of moisture from the air.

In the method described by König,³¹ from ten to 20 grams of the fine earth, properly prepared by air-drying and sifting, for analysis, are heated at 100° to constant weight. For control, five grams are placed in a desiccator over sulfuric acid for two or three days.

The total loss on ignition is made at a low red heat after previous drying at 140°. The sample is then treated with ammonium carbonate solution, evaporated on the water-bath, gently ignited and the operation repeated until constant weight is obtained. This is done to restore any possible loss from the decomposition of carbonates, which as seen above, Petermann does not fear. On the other hand, if large quantities of ferrous oxid be present, it is converted into ferric oxid during ignition and the apparent loss in weight be less than really takes place.

Wolff directs that a small portion of the well-mixed earth, for example, 20 grams, be spread out on a flat zinc plate, and its changes in weight observed through several days. These observations are continued until the variations are so slight that the loss can be determined with sufficient exactness from the last weighings. The soil is then dried at 125° in a hot air-chamber. The loss in weight will give the mean hygroscopic moisture in the soil under the conditions in which the experiment is made.

²⁹ Die landwirtschaftlichen Versuchs-Stationen, 1891, 38 : 311.

³⁰ Bulletin 46, Bureau of Chemistry : 71.

³¹ König, Untersuchung landwirtschaftlich und gewerblich wichtiger Stoffe, second edition, 1898 : 15.

331. Loss on Ignition.—The loss on ignition represents any hygroscopic moisture not removed by previous drying, all water in combination with mineral matters as water of constitution, all organic acids and ammoniacal compounds, all organic matter when the ignition is continued until the carbon is burned away, all or nearly all of the carbon dioxid present in carbonates, when the ignition is long continued at a high temperature, and, finally, some of the chlorids of the alkalies, if the temperature have been carried too high or been continued too long.

The loss of carbon dioxid in carbonates may be mostly restored by moistening the ignited mass two or three times with ammonium carbonate, followed by gentle ignition for a few minutes to incipient redness, to remove excess of the reagent. The apportionment of the rest of the loss justly among the remaining volatile constituents of the original sample is a matter of some difficulty but may be approximately effected by the methods to be submitted.

332. Determination of Loss on Ignition.—*Method of the Official Agricultural Chemists.*³² The platinum dish and five grams of soil used to determine the hygroscopic moisture may be employed to determine the volatile matter. Heat the dish and dry soil to low redness. The heating should be prolonged till all organic material is burned away, but below the temperature at which alkaline chlorids volatilize. Moisten the cold mass with a few drops of a saturated solution of ammonium carbonate, dry, and heat to 150° to expel excess of ammonia. The loss in weight of the sample represents organic matter, water of combination, salts of ammonia, etc.

According to Knop³³ the total loss on ignition is determined as follows: About two grams of the fine earth are carefully ignited until all organic matter is consumed. The sample is then mixed with an equal volume of finely powdered, pure oxalic acid, and again heated until all the oxalic acid is melted and finally decomposed. After cooling, the sample is weighed, again mixed with

³² Bulletin 46, Bureau of Chemistry, 72.

³³ König, *Untersuchung landwirtschaftlich und gewerblich wichtiger Stoffe*, 2nd edition, 1898 : 15.

half as much oxalic acid as before, ignited, cooled, weighed, and the process continued until the weight is constant.

The method recommended by König consists in igniting about ten grams of the fine earth at the lowest possible temperature until all the humus is destroyed. Thereafter the sample is repeatedly moistened with a solution of ammonium carbonate and ignited after drying at 100° , until constant weight is obtained. In soils rich in carbonates some carbon dioxide may be lost by the above process. For this a proper correction can be made by estimating the carbon dioxide in the sample, both before and after the execution of the above described process.

The method described by Frühling as much used in the German laboratories, consists in igniting ten grams of the fine earth, previously dried at 140° in a crucible placed obliquely on its support and with the cover so adjusted over its mouth as to give a draft within the body of the crucible. The ignition, at a gentle heat is continued until on stirring with a platinum wire no evidence of unconsumed carbon is found. The moistening with solution of ammonium carbonate, should not take place until the contents of the crucible are cool. Subsequent ignition, at a low heat for a short time, will remove the excess of ammonium salt.

333. Method of Berthelot and André.³⁴—The earth dried at 110° contains still a greater or less quantity of combined water. The water united with alumina, silica and certain salts is meant, but not the water of constitution belonging to organic bodies. The exact estimation of this water offers many difficulties. The total loss obtained at a red heat embraces:

(1) The water combined with zeolitic silicates, with alumina and with organic compounds:

(2) The water produced by the combustion of the organic compounds:

(3) The carbon dioxide resulting from the partial decomposition of the calcium and magnesium carbonates:

(4) The carbon burned and the nitrogen lost during ignition. The measure of the loss of weight in an earth heated to redness

³⁴ Annales de Chimie et de Physique, 1892, [6], 25 : 289, et seq.

in contact with the air is not therefore, an exact process of estimating water or even volatile matters.

A better defined result is obtained in carefully burning a known weight of earth either in a current of free oxygen, or with lead chromate. The water produced in such a combustion is secured in a U-tube filled with pumice stone saturated with sulfuric acid, the carbon dioxid being absorbed afterwards in potash bulbs and by solid potash. The weight of earth burned is chosen so as to furnish a convenient weight of both water and carbon dioxid. In general about five grams are sufficient. When the combustion is made with oxygen, the soil is contained in a boat and the products of the combustion are carried over a long column of copper oxid heated to redness. The residue left in the boat is weighed at the end of the operation, and in this residue it is advisable to determine any undecomposed carbonate. Should the sample burn badly and be mixed with carbonaceous matter at the end of the operation, it will be necessary to substitute the lead chromate method. In this case, of course, the residue left after combustion is not weighed. Whichever method is employed gives a quantity of water originally combined with the soil, plus the quantity arising from the combustion of the hydrogen of the organic matter. The details of the processes for organic combustion will be given in a subsequent part of this manual. It is not possible to divide the water between these two sources directly, but this can be done by calculation, which gives results lying within the limits of probability. The method follows:

The organic nitrogen, determined separately, by soda-lime, the method of Kjeldahl, or volumetrically, is derived from proteid principles resembling albuminoids containing about 16% of nitrogen. The nitrates contained in the earth are in such feeble proportion, as to be negligible in this calculation. The total weight of these nitrogenous principles in the soil is therefore easily calculated. The carbon contained in the proteids is then calculated on a basis of 53 per cent of their total weight, and the hydrogen on a basis of 7.2 per cent. From the weight of the total organic carbon (determined as described further on) is subtracted the carbon present in the proteids. The remainder corresponds to the

organic carbon present as carbon hydrates, (ligneous principles containing 44.4 per cent carbon and 6.2 per cent hydrogen). By adding together the weight of the hydrogen contained in the ligneous principles, and the hydrogen contained in the proteids, and multiplying the sum by nine, the weight of water formed by the combustion of all the organic matter in the sample is obtained. This is subtracted from the weight of the total water obtained by *direct determination as described above*. The difference represents the weight of water combined with the minerals, etc., as well as with organic matters.

334. Method of van Bemmelen.³⁵—According to the view of van Bemmelen, the soil contains colloidal humus and colloidal silicate, which complicate the determination of water. The colloids retain water in varying quantities, depending upon the following conditions:

- (1) Upon their composition and state of molecular equilibrium.
- (2) Upon the pressure of the aqueous vapor.
- (3) Upon the temperature.

At each degree of temperature, the quantity of absorbed water which a colloid can retain in a space saturated with aqueous vapor, is different. The quantity of water which air-dried earth gives off at 100°, has therefore, no special significance unless all conditions are known.

In addition to the estimation of the quantity of water which soils, in their natural condition, are capable of taking up and holding, at ordinary temperatures, the estimation of the quantity of water which they can take up in different temperatures in spaces saturated with aqueous vapor should be of interest. It follows, therefore, that there is no special value in data obtained by drying earth at 100° or 110°. For the purpose of comparison, it is preferable to select that point at which the soil is dried over sulfuric acid, the point at which the tension of the water vapor in the soil, at a temperature near 15°, approaches zero. The water which still remains in the soil under these conditions is characterized as firmly combined water.

³⁵ Die landwirtschaftlichen Versuchs-Stationen, 1891, 38 : 279, et seq.

Van Bemmelen truly observes that only in soils which contain no carbonates and no chlorids and sulfids, can the loss on ignition be regarded as the sum of the humus and water content. By moistening with ammonium carbonate, the correction for expelled carbon dioxid cannot be correctly made as has been supposed up to the present time. In the first place, ignited magnesia, when it has lost its carbon dioxid, does not take this up completely on moistening with ammonium carbonate; in the second place, reactions with the chlorids may take place; and in the third place, the lime which is in the humus will be converted into calcium carbonate. Chlorids on ignition may be volatilized or oxidized. The sulfuric acid formed from the sulfids, on ignition, can expel carbon dioxid; further than this the iron of pyrites takes up oxygen on ignition. All these influences make the numbers obtained from loss on ignition extremely variable.

With sea slime van Bemmelen has weighed the soil after the elementary analysis and estimated, in addition to the carbon dioxid, both chlorin and sulfuric acid therein. The comparison of these estimations with those of CO_2 , Cl , SO_3 and S , made in the original soil, gave the necessary corrections; viz., for the increase in the weight through oxidation of sulfur and iron, and for the decrease in weight through the volatilization of sodium chlorid, sulfur, and carbon dioxid. A trace of chlorin was evolved as ferric chlorid, nevertheless, the molecular weight of sodium chlorid, 58.5 is scarcely different from the equivalent quantity of ferric chlorid, $\frac{1}{6}$ of 325 viz., 54. For this reason the estimation of loss of water, on ignition, of sea slime is less exact than that of soils which are free from carbonates and sulfids and which, as is usually the case with tillable soils, contain only small quantities of chlorids and sulfates.

The Strongly Combined Water.—Water which, at a temperature of near 15° , in a dry atmosphere, still remains in the soil, is chiefly combined according to van Bemmelen with the colloidal bodies therein. Its estimation presents, naturally, difficulties and is not capable of any great exactness. The quantity of strongly combined water, on the one hand is determined from the difference between the loss on ignition and the quantity of humus pres-

ent, calculated from the content of carbon; and on the other hand, from the difference between the water obtained by elementary analysis and the water which corresponds to the calculated quantity of humus. If the hydrogen content of humus is correctly taken and no appreciable error is introduced through the factor 1.724, both of these differences must agree. On the other hand the hydrogen content of the humus can be computed from the difference between the water found and the calculated content of the firmly combined water.

The hydrogen content of humus bodies, dried at 100°, varies between four and five per cent. Eggertz has found the content from 4.3 to 6.6 per cent of hydrogen in 13 soils which he first treated with dilute hydrochloric acid then extracted with ammonia or potash lye and precipitated this alkaline extract with acid. The method of applying these principles to soil analysis is indicated in the following scheme:

A volcanic earth from Deli gave, on elementary analysis:

	Per cent.
Carbon	2.94
Water	14.78
Nitrogen	0.28
Loss on ignition.....	17.54

FIRST CALCULATION.

Loss on ignition.....	17.54
Humus = carbon, $2.94 \times 1.724 =$	5.07
Difference = firmly combined water.....	12.47

Assuming that a humus dried over sulfuric acid contains five per cent of hydrogen, the second calculation is made as follows.

SECOND CALCULATION.

$5.07 \text{ humus} \times 5 \text{ per cent.} = 0.253 \text{ per cent. of hydrogen in humus corresponding to } 2.28 \text{ per cent. of water.}$

	Per cent.
Water found	14.79
Difference = firmly combined water	12.51

THIRD CALCULATION.

Firmly combined water.....	12.47
Water from the hydrogen in humus	2.28
Total water	14.75
Found.....	14.79

In this way, in three other volcanic earths and in an ordinary

alluvial clay from Rembang, there were found by analysis and by calculation the following percentages of water:

	1.	2.	3.	4.	5.
Percentage of water calculated..	14.75	7.74	8.06	4.90	6.01
" " " found.....	14.79	7.63	8.05	4.70	6.00

On the contrary, when the calculation is made from sea-slime taken from under the water a higher content of hydrogen must be assumed; *viz.*, about six per cent. In two samples of sea-slime calculated in this way the following numbers were obtained:

Percentage of water calculated	8.61	3.71
" " " found	8.53	3.57

It is, therefore, quite evident that the organic compounds of soil taken from under the sea-water are richer in hydrogen than those exposed to the air or in cultivation.

335. Uniform Conditions of Desiccation.—It is evident from the foregoing discussion that the exact determination of water in soils, in its various forms of combination, is a difficult analytical problem. Slight variations in temperature, or in form of drying apparatus or in lengths of time the sample is submitted to desiccation or in the pressure of the air and its degree of saturation will influence more or less the final results. A general agreement among chemists in respect of all these details would at least lead to uniformity of results and possibility of comparison. Among many other valuable suggestions which have been made in this respect attention may be called to the observations of Puchner,³⁶ who points out the imperfections of some of the methods employed and prefers the electrical drying oven as more reliable when desiccation at 105° is desired.

336. Determination of Moisture by Electrical Methods.—The method proposed by Whitney for the estimation of water in the soil by electrical methods has been worked out by Briggs.³⁷

This method is based on the principle that the resistance offered to the passage of an electrical current from one electrode to another when buried in the soil, varies with the amount of water in the soil. The electrical resistance is very nearly inversely proportional to the square of the water content expressed in percent-

³⁶ Die landwirtschaftlichen Versuchs-Stationen, 1901, 55 : 309.

³⁷ Division of Soils, Bulletin No. 15.

age of the weight of the soil. In these measurements it is necessary to maintain the temperature and the amount of salt in solution constant or to correct for their variations. The character of the salt solution must also be taken into account.

It is evident from a statement of the conditions of the problem that more time is required to determine the nature of the environment and to make the various determinations than would be required to ascertain the content of moisture by the usual drying process. Moreover, the standardization of the apparatus is secured by actual determinations of moisture by drying. Even granting the reliability of the process its practical application is not apparent. For the description of the instruments employed and the details of the manipulation, the original paper should be consulted.

337. General Conclusions.--In the foregoing paragraphs have been collected the most widely practiced methods of determining moisture in soil in both a free and combined state. The following conclusions may serve to guide the analyst who endeavors to determine the water in any or all of its conditions:

(1) The samples should be secured in such a way as to be representative of the actual moisture conditions and each sample be accompanied by recent meteorological data and the samples secured in great numbers over widely scattered areas. These samples should be dried at from 100° to 110° for rapid work, or where time can be spared may be air-dried.

(2) For a simple determination of the water left in the soil after air-drying (hygroscopic water) the method of the Association of Official Agricultural Chemists may be followed. There is much difference of opinion in respect of the proper temperature at which this moisture is to be determined. Much here depends on the nature of the soil. An almost purely mineral soil may safely be dried at 140° or 150°. A peaty soil, on the contrary, should not be exposed to a temperature above 100°. For general purposes the temperature chosen by the official chemists is to be recommended.

(3) Water of composition can only be determined by ignition. As has been fully shown, this process not only eliminates the water,

but also destroys organic matter, decomposes carbonates and sulfids, and, to some extent, chlorids. Subsequent repeated treatment with ammonium carbonate may restore the loss due to carbon dioxide, but in many cases not entirely. The water which comes from organic matter may be approximately calculated from the humus content of the sample, but as will be seen further on, the methods of estimating humus are only approximate. Nevertheless, in distributing the losses on ignition properly to the several compounds of the soil there is no better method now known than that of taking into consideration the humus content and carbonates present. The principles of procedure established by Berthelot and André, and van Bemmelen, are to be applied in all such cases, modified as circumstances may arise according to the judgment of the analyst.

338. Estimation of the Organic Matter of the Soil.—The organic matter in the soil may be divided into two classes. First, the undecayed roots and other remains of plant and animal life, and the living organisms existing in the soil. The study of the organisms which are active in the condition of plant growth will be the subject of a special chapter. Second, the decayed or partially decayed remnants of organic matter in the soil known as humus. Such matter may be present in only minute traces, as in barren sand soils, or it may form the great mass of the soil under examination, as in the case of peat, slime, and vegetable mold. It is with the investigation of the second class of matter that the analyst has chiefly to do at present. The problems which are to be elucidated by the analytical study of such bodies are the following: (1) The total quantity of such matter in the soil. (2) The determination of the organic carbon and hydrogen therein. (3) The determination of total nitrogen. (4) The determination of the availability of the nitrogen for plant growth. (5) The estimation of the humic bodies (humus, humic acid, ulmic acid, etc.).

The importance of humus in the promotion of plant growth is sufficient excuse for the somewhat extended study of the principles which underlie the analytical methods, and the methods themselves, which follow.

339. Total Quantity of Organic Matter.—The total approximate quantity of organic matter in the soil can be determined by simple ignition, in the manner noted in the following paragraphs. When the proper correction for free and combined water is applied, and for carbonates and volatile chlorids, by the copper oxid or lead chromate combustion of the sample, the approximate total of the organic matter of all kinds is obtained.

340. Estimation of the Organic Carbon.—To estimate the organic carbon in a soil the sample may be burned in a current of oxygen, or after mixing with lead chromate.

In a Current of Oxygen.—When burned in a current of oxygen the sample is held in a boat and the gases arising from the combustion directed over copper oxid at a red heat. The carbon thus disappears as carbon dioxid and is absorbed and weighed in the usual way.

With Lead Chromate.—The lead chromate employed should be previously tested since it often contains other compounds, especially lead acetate and nitrate, furnishing in the one case both carbon dioxid and water, and in the other gaseous nitrogen compounds.

From two to ten grams of earth, according to its richness in organic matter, are used in the combustion. The total carbon dioxid is obtained in this process both from carbonates and organic bodies. The water and carbon dioxid are secured and weighed in the usual manner employed in ultimate organic analysis.

The oxygen method should be used in all cases possible. Although it does not always give the whole of the carbon dioxid present as carbonates, the rest can be easily estimated by treating the residue in the boat with hydrochloric acid, in an apparatus for estimating that gas.

Calculation of Results.—The whole of the carbon dioxid is determined either as has been indicated by direct combustion with lead chromate, or by taking the sum of the amounts by burning in a stream of oxygen and treating the residue in a carbon dioxid apparatus.

The carbon dioxid contained in the original carbonates should

be determined by direct treatment of the sample with acids in the usual way.

The carbon in organic compounds is determined by subtracting the carbon present as carbonates from the total.

From the organic carbon contained in the soil the humus is calculated on the supposition that it contains 58 per cent of carbon. It is, therefore, only necessary to multiply the percentage of carbon found by 1.724, or the carbon dioxid found by 0.471, to determine the quantity of humus in the dried soil.

341. **Details of the Direct Estimation of Carbon in Soils by Various Methods.**—(1) *Oxidation by Chromic Acid.*—The method of Wolff by oxidation with chromic acid has been worked out in detail by Warington and Peake.³⁸ It consists in treating the soil with sulfuric acid and potassium bichromate, or by preference with a mixture of sulfuric and chromic acids, the carbon dioxid evolved being estimated in the usual way. This method is recommended by Fresenius as an alternative to a combustion of the soil with copper oxid or lead chromate. It is apparently the method which has been most generally employed in agricultural investigations.

Ten grams of the finely powdered soil are placed in a flask of about 250 cubic centimeters capacity, provided with a caoutchouc stopper, through which pass two tubes, one for the supply of liquids, the other for the delivery of gas. The soil is treated with 20 cubic centimeters of water and 30 cubic centimeters of oil of vitriol, and the whole, after being thoroughly mixed, is heated for a short time in a water-bath, the object in view being the decomposition of any carbonates existing in the soil. Air is next drawn through the flask to remove any carbon dioxid which has been evolved. The stopper is next removed, and coarsely powdered potassium bichromate introduced. In the case of a soil containing three per cent of carbon, six grams of bichromate will be found sufficient, a portion remaining undissolved at the end of the experiment. The stopper is then replaced, its supply-tube closed by a clamp, and the delivery-tube connected with a series of absorbents contained in U-tubes. The first of these tubes contains solid

³⁸ Journal of the Chemical Society, London, 1880, 38 : 761 et seq.

calcium chlorid; the second, fragments of glass moistened with oil of vitriol; the third and fourth are nearly filled with soda-lime, a little calcium chlorid being placed on the top of the soda-lime at each extremity. The last named tubes are for the absorption of carbon dioxid, and have been previously weighed. The series is closed by a guard-tube containing soda-lime, with calcium chlorid at the two ends.

The flask containing the soil and bichromate is now gradually heated in a water-bath, the contents of the flask being from time to time mixed by agitation. A brisk reaction occurs, carbon dioxid being evolved in proportion as the soil is rich in organic matter. The temperature of the water-bath is slowly raised to boiling as the action becomes weaker, and is maintained at that point till all action ceases. As bubbles of gas are slowly evolved for some time, it has been usual in these experiments to prolong the digestion for four or five hours. When the operation is concluded the source of heat is removed, an aspirator is attached to the guard-tube at the end of the absorbent vessels, and air freed from carbon dioxid is drawn through the flask and through the whole series of U-tubes. The U-tubes filled with soda-lime are finally weighed, the increase in weight showing the amount of carbon dioxid produced. The object of the calcium chlorid placed on the surface of the soda-lime is to retain the water which is freely given up when the soda-lime absorbs carbon dioxid. The second U-tube filled with soda-lime does not gain in weight till the first is nearly saturated; it thus serves to indicate when the first tube requires refilling. The same tubes may be used several times in succession.

No increase in the carbon dioxid evolved is obtained by substituting chromic acid for potassium bichromate.

The organic matter of the soil appears to the eye to be completely destroyed by the digestion with sulfuric acid and potassium bichromate; the residue of soil remaining in the flask when washed with water is perfectly white, or the dark particles, if any, are found to be unaltered by ignition, and therefore to be inorganic in their nature. Under these circumstances considerable confidence has naturally been felt in this method. The complete destruction of the humic matter of the soil does not, however, nec-

essarily imply that the carbon has been entirely converted into carbon dioxid as has been pointed out by Wanklyn. According to his demonstration of the action of chromic acid on organic matter the oxidation frequently stops short of the production of carbon dioxid. While oxidation with chromic acid apparently leads to a complete reaction when the carbon is in the form of graphite, it would probably yield other products than carbon dioxid when the carbon exists as a carbohydrate. The doubt thus raised as to the correctness of the results yielded by the chromate method makes it desirable to check the work by the use of other methods for the determination of carbon. For this purpose Warrington and Peake recommend:

(2) *Oxidation with Potassium Permanganate.*—In the trials with this method ten grams of soil are digested in a closed flask with crystals of potassium permanganate, and a measured quantity of solution of caustic potash containing five grams of potash for each 20 cubic centimeters. Seven grams of the permanganate are found to be sufficient for a soil containing 3.3 per cent of carbon. The flask is heated for half an hour in boiling water, and then for one hour in a salt-bath. The flask during this digestion is connected with a small receiver containing a little potash solution, to preserve an atmosphere free from carbon dioxid. Distillation to a limited extent is allowed during the digestion in the salt-bath.

The first part of the operation being completed a rubber stopper, carrying a delivery and supply-tube, is fitted to the flask, which is then connected with the system of U-tubes already described. Dilute sulfuric acid is then poured down the supply-tube, a water-bath surrounding the flask is brought to boiling, and maintained thus for one hour, after which air, free from carbon dioxid, is drawn through the apparatus, the U-tubes containing soda-lime being finally disconnected and weighed.

In the first stage of this method the carbon of the organic matter is converted into carbonate, and probably also into potassium oxalate.³⁹ In the second stage the oxalate is decomposed by the sulfuric acid and permanganate, and the carbon existing, both as

³⁹ Wanklyn, *Philosophical Magazine*, 1878, [5], 5 : 466.

oxalate and carbonate, is evolved as carbon dioxid, and absorbed by the weighed soda-lime tubes. Both F. Schulze and Wanklyn have employed potassium permanganate for the determination of organic carbon, but they have preferred to calculate the amount of carbon from the quantity of permanganate consumed, as, however, by so doing everything oxidizable by permanganate is reckoned as carbon, it seems better to make a direct determination of the carbon dioxid formed.

From the amount of carbon dioxid found, is to be subtracted that existing as carbonates in the soil, and in the solution of potash used. For this purpose an experiment is made with the same quantities of soil and potash previously employed, but without permanganate, and the carbon dioxid obtained is deducted from that yielded in the experiment with permanganate. If the potash used contains organic matter two blank experiments will be necessary, one with potash and permanganate, and one with soil alone.

A further difficulty arises from the presence of chlorids in the materials, which occasions an evolution of free chlorin when the permanganate solution is heated with sulfuric acid. This error occurs also with the chromic acid method, but in that case the quantity of chlorid is merely that contained in the soil, which is usually very small; in the permanganate method we have also the chlorid present in the caustic potash, and this is often considerable. Corrections for chlorin by blank experiments are unsatisfactory, the amount of chlorin which reaches the soda-lime tubes depending in part on the degree to which the calcium chlorid tube has become saturated with chlorin. It is better therefore to remove the chlorin in every experiment by the plan which Perkin has suggested, by inserting a tube containing silver foil, maintained at a low red heat, between the flask and the absorbent U-tubes.

The amount of carbon dioxid yielded by oxidation with potassium permanganate is found to be considerably in excess of that obtained by oxidation with chromic acids. To ascertain whether these higher results really represented the whole of the carbon present in the soil, trials were next made by actual combustion of the soil in oxygen.

(3) *Combustion in Oxygen.*—The most convenient mode of carrying out the combustion of soil is to place the sample in a platinum boat, and ignite it in a current of oxygen in a combustion tube partly filled with cupric oxid. A wide combustion tube is employed, about 20 inches long, and drawn out at one end; the front of the tube is filled for eight inches with coarse cupric oxid, the hind part is left empty to receive the platinum boat. The drawn out end of the combustion tube is connected with a series of absorbent U-tubes, quite similar to those employed for the estimation of carbon dioxid in the chromic acid method. Between these absorbent vessels and the combustion tube is placed a three-bulbed Geissler tube filled with oil of vitriol. The oil of vitriol is quite effective in retaining nitrous fumes. The wide end of the combustion tube is connected with a gas-holder of oxygen; the oxygen gas is made to pass through a U-tube of soda-lime before entering the combustion tube, to remove any possible contamination of carbon dioxid.

In starting a combustion the part of the combustion tube containing the cupric oxid is brought to a red heat, and oxygen is passed for some time through the apparatus. Ten grams of soil, previously dried, are placed in a large platinum boat, which is next introduced at the wide end of the combustion tube. The combustion is conducted in the usual manner, a current of oxygen being maintained throughout the whole operation. It is very useful to terminate the whole series of absorbent vessels with a glass tube dipping into water; the rate at which the gas is seen to bubble, serves as a guide to the supply of oxygen from the gas-holder, the consumption of oxygen varying, of course, with different soils, and at different stages of the combustion. At the close of the combustion, oxygen, or air freed from carbon dioxid, is passed for some time through the apparatus to drive all carbon dioxid into the absorbent vessels. One experiment can be followed by another as soon as the hind part of the combustion tube has cooled sufficiently to admit a second platinum boat. The same combustion tube can be employed for several days, if packed in the usual manner in asbestos.

The presence of carbonates in the soil occasions some difficulty in working the combustion method, as a part of this carbon dioxid

will, of course, be given up on ignition, and be reckoned as carbon. The simplest mode of meeting this difficulty is to expel the carbon dioxid belonging to the carbonates before the combustion commences. The method of Manning; namely, treatment with a strong solution of sulfurous acid, may be employed for this purpose. The ten grams of soil taken for combustion are placed in a flat-bottomed basin, covered with a thin layer of the solution of sulfurous acid, above mentioned, and frequently stirred. After a time the action is assisted by a gentle heat. When the carbonates have been completely decomposed the contents of the basin are evaporated to dryness on a water-bath; the dry mass is then pulverized, and removed to the platinum boat for combustion in oxygen. For the action of the sulfurous acid to be complete it is essential that the carbonates should be in very fine powder, since even chalk is but imperfectly attacked when present in coarse particles.

342. Comparison of Methods.—A considerable number of soils analyzed by the chromic acid method and by the combustion method, by Warrington and Peake, with the assistance of Cathcart, show the following comparisons:

PERCENTAGE OF CARBON FOUND BY TWO METHODS IN SOILS DRIED
AT 100°.

No.	Kind of soil.	Chromic acid method.			Combustion in oxygen method.			Per cent. yielded by chromic acid.
		Exp. 1.	Exp. 2.	Mean.	Exp. 1.	Exp. 2.	Mean.	
1.	Old pasture...	2.85	2.79	2.82	3.58	3.55	3.57	79.0
2.	" " ...	2.83	2.79	2.81	3.57	3.53	3.55	79.1
3.	" " ...	2.76	2.76	2.76	3.46	3.46	3.46	79.7
4.	" " ...	2.74	2.76	2.75	3.37	3.38	3.38	81.4
5.	" " ...	2.64	2.54	2.59	3.31	3.36	3.34	77.5
6.	" " ..	2.51	2.43	2.47	3.15	3.15	3.15	78.4
7.	" " ...	2.40	2.44	2.42	3.09	3.13	3.11	77.8
8.	New pasture..	1.92	1.93	1.93	2.41	2.40	2.41	80.1
9.	" " ..	1.66	1.81	1.74	2.39	2.43	2.41	72.2
10.	Arable soil....	1.78	1.78	1.78	2.14	2.13	2.14	83.2
11.	" "	1.21	1.14	1.18	1.40	1.43	1.42	83.1
12.	Subsoil	0.28	0.27	0.28	0.37	0.38	0.38	73.7

Of the above soils the arable soils, Nos. 10 and 11, were the only ones containing carbonates in any quantity exceeding a min-

ute trace. The two soils in question were treated with sulfurous acid before combustion, the others not.

All the determinations with chromic acid give distinctly lower results than on combustion in oxygen. Excluding analyses nine and 12, which were not made under the same conditions as the others, the relation of the carbon found by the two methods is tolerably constant, the average being 79.9 of carbon found by oxidation with chromic acid for 100 yielded by combustion in oxygen. The results obtained by the chromic acid method thus appear to be very considerably below the truth.

Four typical soils were analyzed by the permanganate, as well as by the chromic acid and combustion methods. The results obtained are as follows:

PERCENTAGE OF CARBON FOUND BY THREE METHODS IN SOILS DRIED AT 100°.

Kind of soil.	Combustion method.	Chromic acid method.	Permanganate method.			Yielded by permanganate if carbon by combustion = 100.
	Mean. Per cent.	Mean. Per cent.	Exp. 1. Per cent.	Exp. 2. Per cent.	Mean. Per cent.	Per cent.
Old pasture.....	3.55	2.81	3.26	3.30	3.28	92.4
New pasture.....	2.41	1.93	2.29	2.30	2.30	95.4
Arable soil.....	1.42	1.18	1.28	1.33	1.31	92.3
Subsoil.....	0.38	0.28	0.34	0.34	0.34	89.5

Oxidation by permanganate thus gives a much higher result than oxidation with chromic acid; but even the permanganate fails to convert the whole of the carbon into carbon dioxide, the product with permanganate being on an average of the four soils 92.4 per cent of that yielded by combustion in oxygen.

Wanklyn states that a temperature of 160°-180° is necessary in some cases to effect complete oxidation with permanganate and caustic potash. Such a temperature is found impracticable when dealing with soil, from the action of the potash on the silicates present; hence possibly the low results obtained.

Combustion in oxygen appears from these experiments to be the most satisfactory method for determining carbon in soil, nor is this method, on the whole, longer or more troublesome than the other methods investigated.

Warrington and Peake have further determined the loss on ignition of the four soils mentioned above, with a view of comparing

this loss with the amount of organic matter calculated from the carbon actually present. In making this calculation they have taken as the amount of carbon in the soil, that found by combustion in oxygen, and have assumed with Schulze, Wolff, and Fresenius, that 58 per cent of carbon will be present in the organic matter of soils. The four soils were heated successively at 100°, 120°, and 150°, till they ceased to lose weight; the loss on ignition in each of these stages of dryness is shown in the following table:

PERCENTAGE LOSS ON IGNITION COMPARED WITH ORGANIC MATTER
CALCULATED FROM CARBON.

Kind of soil.	Between 100° and ignition. Per cent.	Between 120° and ignition. Per cent.	Between 150° and ignition. Per cent.	Organic matter at 58 per cent. carbon. Per cent.
Old pasture	9.27	9.06	8.50	6.12
New pasture	7.07	6.88	6.55	4.16
Arable soil	5.95	5.70	5.61	2.44
Clay subsoil	5.82	5.39	4.76	0.65

The loss on ignition is seen to be in all cases very considerably in excess of the organic matter calculated from the carbon, even when the soil has been dried at as high a temperature as 150°. The error of the ignition method is least in soils rich in organic matter, as, for instance, the old pasture soil in the above table. The error reaches its maximum in the case of the clay subsoil, which contains very little carbonaceous matter, but is naturally rich in hydrated silicates, which part with their water only at a very high temperature.

The above methods of Warington and Peake have been given in detail, and in almost the verbiage of the authors for the reason that the working directions are clearly set forth, and may serve, therefore, as guides to the previous methods where only general indications of manipulation have been given.

343. Modification of Cameron and Brazeale.—In this method the combustion apparatus is arranged as shown in Fig. 76.⁴⁰

The combustion is effected in a round-bottomed flask *F*, of about 400 cc. capacity, fitted with a three-hole rubber stopper. The stopper is fitted with a dropping funnel, a tube for the introduction of air previously freed from carbon dioxide by bub-

⁴⁰ Journal of the American Chemical Society, 1904, 26 : 29.

bling through a solution of potassium hydrate in the flask *G*, and a tube leading through a condenser to a train of absorption bulbs. This train contains, first, a Peligot tube *A*, containing a saturated and slightly acidified solution of silver sulfate to absorb both hydrochloric acid and sulphur trioxid or dioxid should they be generated; then a guard tube *B*, containing concentrated sulfuric acid, followed by a potash bulb *C*, and an acid bulb *D*, to be weighed with the potash bulb. An acid guard bulb *E* completes the train. The whole apparatus is attached to an aspirator,

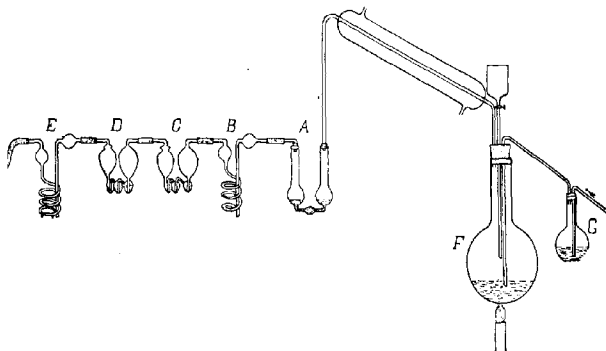


Fig. 76. Apparatus for determining organic matter by chromic acid method.

so that air free from carbon dioxid can be drawn through the combustion flask and train. The procedure is as follows:

A sample of the soil, usually about ten grams, is placed in the flask *F*. From five to ten grams of pulverized potassium bichromate are then added, and the whole mixed thoroughly by shaking, care being taken to prevent any of the mixture adhering to the sides of the flask above the level of the liquid. The flask is closed and a gentle stream of air drawn through the apparatus. After about ten minutes, concentrated sulfuric acid (sp. gr. about 1.83) is slowly and cautiously run in by means of the dropping funnel until the tip of the glass tube for the introduction of air is covered. When this point has been reached, and if no very vig-

orous action is taking place, the combustion flask is slowly heated until the sulfuric acid commences to give off fumes. It is held at this temperature for from five to ten minutes, and then allowed to cool slowly, unless there is reason to believe combustion has not been complete, in which case the temperature is again raised. During this time a current of air is kept passing through the apparatus. It is advisable to have the bulb of the dropping funnel empty before commencing the heating, so that the tube can be quickly opened, in case of danger of a sudden evolution of gas. In case the sample contain large amounts of chlorid, it is suggested that they be first heated with sulfuric acid until the chlorids are decomposed before the potassium chromate is added. If the potassium chromate be dissolved in the acid instead of being added in a powdered state to the soil the tendency to evolve chlorine appeared to be checked. No satisfactory reason for this is offered.

344. Method of Messinger.—In order to avoid the loss in carbon dioxid that attends the moist combustion of an organic body in chromic-sulfuric acid, Messinger has suggested the interposition of a short combustion tube between the flask where the decomposition takes place and the absorbing system where the carbon dioxid is collected.⁴¹

The process is based on the assumption the gaseous carbon compounds arising during the moist combustion are not composed exclusively of carbon dioxid, but may contain small quantities of carbon monoxid and hydrocarbons. To convert these compounds into carbon dioxid all of the gaseous products of combustion freed as completely as possible from water by passing through a condenser set obliquely on the neck of the combustion flask, are conducted through a combustion tube heated to low redness and filled with a mixture of copper oxid and lead chromate. The carbon compounds, now all converted into carbon dioxid, are absorbed in the usual way. To set up an apparatus of this kind the analyst should consult the figure in the second paper cited above.

345. Estimation of Organic Hydrogen.—The estimation of the total hydrogen is made without difficulty either by burning the

⁴¹ *Berichte der deutschen chemischen Gesellschaft*, 1888, **21** : 2910, 1890, **23** : 2756.

sample in a current of oxygen or with pure lead chromate, and weighing the water produced. This water comes from two sources, the pre-existing water and organic hydrogen. There is no direct method of distinguishing one from the other. They may however, be estimated indirectly. The method of calculating the organic hydrogen has already been given (paragraph 333). Experience shows that the hydrogen thus calculated is a little greater than is necessary to form water with the whole of the oxygen found by 6.25, plus 6.2 per cent of the other organic carbon com-

The organic hydrogen is equivalent to 7.2 per cent of the nitrogeous constituents of the soil obtained by multiplying the nitrogen found by 16.25, plus 6.2 per cent of the other organic carbon compounds present calculated on the assumption that they contain 44.4 per cent of carbon. Thus, one gram of a soil that contains one per cent of protein and three per cent ligneous (carbohydrate) matter would contain

$$\begin{aligned} &.01 \times .072 + .03 \times .062 \\ &= .00258 \text{ gram of hydrogen,} \\ &\text{or } 2.58 \text{ milligrams.} \end{aligned}$$

346. Estimation of Organic Oxygen.—The determination of this oxygen cannot be made directly. It is obtained by calculation, according to Berthelot and André, from the oxygen in the proteid and ligneous matters, as follows:

Let p represent the weight of the proteid bodies in a sample of soil.

$$\text{Then } O = \frac{p \times 33.5}{100}.$$

Let p' = weight of ligneous bodies.

$$\text{Then } O' = \frac{p' \times 49.4}{100} \text{ and the total oxygen} = O + O'.$$

An approximate result is thus obtained, very useful to have when account is taken of the oxidizing processes which go on in the soil during agricultural operations.

347. Estimation of Humus (Matière Noire).—A common method of determining this substance is due to Grandeau.⁴² The

⁴² *Traité d'Analyse des Matières agricoles*, 3rd edition, 1897, 1 : 151.

soil is prepared for analysis by washing with dilute hydrochloric acid of a strength proportional to the quantity of carbonate. Where only a trace of carbonate exists acid of $\frac{1}{500}$ normal strength will suffice. After all the lime has been removed the acid is washed out with water and the washed soil is air-dried. The rest of the operation is carried on as follows: Ten grams of the fine earth, prepared as above, are mixed with coarse sand previously washed with acids and ignited. The mixture is placed in a small funnel, the bottom of which is filled with fragments of glass or porcelain. The mass is moistened with ammonia diluted with an equal volume of distilled water, and allowed to digest for three or four hours. The ammonia dissolves the humus without attacking the silica. The ammoniacal solution is displaced by treating the mass with pure water, or water to which some ammonia has been added, and the whole of the humus is thus obtained in a volume of from twenty to fifty cubic centimeters of filtrate. The filtrate is evaporated to dryness in a weighed platinum dish, and the weight of residue is determined and the percentage of humus calculated therefrom. The residue is incinerated, and when in sufficient quantity the phosphoric acid is determined in the ash. In soils poor in humus a larger quantity than ten grams may be used. If the soil be previously treated with hydrochloric acid, Grandeau recommends that the phosphoric acid be determined always in the ash of the dark matter.

The method has undergone various modifications and, as given by Hilgard, is now practiced as follows:⁴³

About ten grams of soil are placed in a prepared filter. The soil should be covered with a piece of paper (a filter) so as to prevent it from packing when solvents are poured on it. It is now treated with hydrochloric acid from five-tenths per cent to one per cent strong (twenty-five and one-third cubic centimeters of strong acid and 808 cubic centimeters of water) to dissolve the lime and magnesia which prevent the humus from dissolving in the ammonia. Treat with the acid until there is no reaction for lime; then wash out the acid with water to neutral reaction. Dissolve the humus with weak ammonia water, prepared by diluting common satu-

⁴³ Bulletin 38, Division of Chemistry : 85.

rated ammonia water (178 cubic centimeters of ammonia to 422 cubic centimeters of water). Evaporate the humus solution to dryness in a weighed platinum dish at 100°; weigh, then ignite; the loss of weight gives the weight of humus.

The residue from ignition is carbonated with carbon dioxide, heated and weighed, thus giving the ash. It is then moistened with nitric acid and evaporated to dryness. The residue is treated with nitric acid and water, allowed to stand a few hours, and the solution filtered from the insoluble residue, which is ignited and weighed, giving the silica.

The soluble phosphoric acid is determined in the solution by the usual method, as magnesium pyrophosphate. It usually amounts to a fraction, varying from one-half to as little as one-tenth of the total in the soil. While the phosphoric acid so determined is manifestly more soluble and more available to vegetation than the rest of that found by extraction with stronger acid, it is clearly not as available as that which, when introduced in the form of superphosphates, exerts such striking effects even though forming a much smaller percentage of the whole soil. Nevertheless, very striking agreement in respect of the assimilation of phosphoric acid with actual practice is often found in making this determination.

The estimation of humus by combustion, in any form, of the total organic matter in the soil, gives results varying according to the season and having no direct relation to the active humus of the soil.

348. Modification of Grandeau's Method for Determining Humus in Soils.—According to Huston and McBride the function of the vegetable matter in the soil has long been a matter of contention among those interested in the science of agriculture. Two factors have contributed to the uncertainty existing in this matter: First, the very complex and varying nature of the compounds resulting from the decomposition of vegetable matter in the soils; and second, the lack of uniformity in the methods of determining either the total amount of organic matter present in a soil, or the amount that has been so far decomposed as to be of any immediate agricultural value. Prominent among these methods are those in

which a combustion is resorted to, the substance being either burned in air or in a combustion tube with some agent supplying oxygen. The loss on ignition is no measure of the amount of organic matter present since it is practically impossible to remove all the combined water from the soil previous to ignition, and neither of the methods gives information regarding the extent of the decomposition of the organic matter. Pure cellulose and the black matter of a fertile soil are of very different agricultural value.

Determinations of carbon in soils by oxidation with chromic and sulfuric acid, and with alkaline permanganate have been used. The method with alkaline permanganate agrees fairly well with combustion with copper oxid or lead chromate, but the chromic-sulfuric acid method gives only about 80 per cent of the carbon found by the combustion processes. Later investigations since the paper of Huston and McBride was written show that a much higher per cent of the carbon than that mentioned can be obtained by the chromic acid method. However valuable these processes may be for determining the total carbon in the soil, they furnish no information regarding the condition of the carbonaceous soil constituents, and as the determination is really one of carbon, the organic matter must be calculated by using an arbitrary factor. Generally the organic matter of the soil is considered to have 58 per cent carbon; yet different values are given ranging from 40 to 72 per cent.

There is a general opinion that the black or dark brown material of the soil, resulting from the decay of vegetable matter, has a much higher agricultural value than the undecomposed vegetable matter. No very sharp dividing line can be drawn, for changes in the soil are continually going on, and material may be found in almost every stage between pure cellulose and carbon dioxide. The character of the intermediate products will vary according to the conditions of tillage and the supply of air and water.

For agricultural purposes some means of determining the amount of decomposed matter is very desirable. Several solvents have been tried for this purpose. The earlier attempts were made by treating the soil with successive quantities of boiling half-saturated solution of sodium carbonate until the soil appeared to yield

no more coloring matter to the solvent. The solutions were then united, treated with hydrochloric acid, which precipitated the humic acid, which was then washed, dried, and weighed. This was considered the more soluble portion of the humic acid. The soil was afterward treated with caustic potash solution in the same manner, and the humus thus extracted was called insoluble humus. This last process was really more in the nature of manufacturing humus, for sawdust treated with caustic potash yields humic acid, and the inert organic matter in the soil was decomposed to some extent by the caustic alkali. Neither of the processes provided for the separation of the humic acid from the lime, magnesia, alumina, and iron with which it is usually combined in the soil.

In case results of different workers are to be compared, it is of the great importance that methods should be used that are of such a nature that errors resulting from difference of manipulation, and from difficulty of reproducing duplicate work can be reduced to a minimum.

Hence, a simple modification of the Grandeau method has been tried which has the advantage of keeping a definite amount of the soil in contact with a definite volume of ammonia for a fixed time, the strength of the ammonia remaining constant.

The process is as follows: The soil is washed with acid and water as usual. It is then washed into a 500 cubic centimeter cylinder, which is filled to the mark with ammonia of a given strength. The quantity of water used in washing the soil into the cylinder is to be considered in determining the strength of the ammoniacal solution, the cylinder closed and well shaken and allowed to remain for a definite time, usually 36 hours. The material is shaken at regular intervals. The cylinder is left inclined as much as possible without having the fluid touch the glass stopper, thus allowing the soil to settle on the side of the cylinder and exposing a very large surface to the action of the ammonia. During the last 12 hours the cylinder is placed in a vertical position to allow the soil to settle well before taking out the aliquot part of the solution. An aliquot portion of the clear ammoniacal solution is then withdrawn and submitted to analysis.

The process of washing the soil with hydrochloric acid and water is very tedious when performed in the usual way with the

wash-bottle. A simple automatic washing apparatus was devised by which a fixed volume of the washing fluid can be delivered at regular intervals, giving ample time for the thorough draining between each addition of the fluid, and requiring no attention. By this apparatus work can be continued day and night. Instead of washing on the usual form of filter paper in funnels, it is preferable with this apparatus to hold the soils on a disk of filter paper resting on a perforated porcelain disk in the bottom of the funnel. This removes the necessity of washing out the filter papers, does not permit of the accumulation of humus on the edge of the filter paper when the Grandeau process is used, and insures that all the washing fluids pass through the soil and not around it. This form of apparatus reduces the labor to a minimum and permits many determinations to be carried on at once.

This form of apparatus was only lately devised and has only been used long enough to test it and to show its advantages. The reported results were obtained by the ordinary methods of washing.

In all the work reported, five grams were used, as the soils contained so much humus that this amount gave enough humus for good work in the final weighings. The results obtained so far appear in the following tables:

TABLE I.—COMPARISON OF METHOD OF GRANDEAU WITH HUSTON'S MODIFICATION AND OF INFLUENCE OF STRENGTH OF AMMONIA SOLUTION. TIME OF DIGESTION IN MODIFIED METHOD THIRTY-SIX HOURS.

	Two per cent. NH_3 .		Four per cent. NH_3 .		Seven per cent. NH_3 .		Eight per cent. NH_3 .	
	Grand-eau.	Huston.	Grand-eau.	Huston.	Grand-eau.	Huston.	Grand-eau.	Huston.
1. Peat soil	16.40	20.06
Bogus soil	13.98	20.80
" "	17.43
Mean			15.94	20.43				
2. Peat subsoil	13.98	19.38
Bogus "	13.85	20.30
Mean			13.92	19.84				
3. Peat soil	9.05	15.60	14.71	21.24	19.77	21.70	16.05	21.42
Good "	10.27	15.88	15.34	20.20	19.85	21.90	15.40	21.80
Mean	9.61	15.74	15.03	20.72	19.81	21.80	15.73	21.61

4. Peat subsoil	16.75	24.34
Good "	18.60	23.52
Mean.	17.68	23.93
5. Black soil, A	3.90	6.90	(1.86)	7.42
" " "	(1.67)	6.98
" " B	3.88	7.00	4.42
" " "	4.20
Mean.	3.99	6.95	(3.05)	7.20
"	4.31
6. Clay loam.	1.86	4.20	2.40	4.26	2.14	4.02	1.85
West side, A.	4.28
" " B.	1.76	4.36	2.48	(3.40)	2.13	4.48	1.90
" " "	(3.10)
Mean.	1.81	4.28	2.44	(3.76)	2.14	4.25	1.88
"	4.27
7. Clay loam, A.	1.90	4.12	(1.60)	(4.59)
Lysimeter soil, B	1.61	4.22	(1.41)	(4.58)
" " C	1.80	4.12
" " D	1.95	4.04
" " E	1.92	3.85
" " F	1.95	4.08
" " G	1.90	3.93
" " H	1.90	3.80
Mean.	1.76	4.17	(1.80)	(4.12)
"	1.90	3.97

NOTE.—Numbers in parentheses indicate results, generally the earliest ones, which the authors do not consider strictly comparable with the rest of the work. They are given solely for the purpose of exhibiting all the work that has been done to date. When a mean is included in parentheses it indicates that it is calculated from all the results obtained, including those not considered strictly comparable. "Bogus" is a name given to a peaty soil which is very sterile.

TABLE II.—INFLUENCE OF TIME OF DIGESTION. FOUR PER CENT OF AMMONIA USED THROUGHOUT. HUSTON'S METHOD.

	Thirty-six hours.	Forty-eight hours.	Sixty-eight hours.	Ninety-eight hours.
Peat soil.	21.24	22.28	24.04
Good "	20.20	21.70	23.94
Mean	20.72	21.91	23.99
Clay loam	4.28	4.00	4.40
" "	4.26	4.01	4.85
West side	(3.40)
" "	(3.05)
Mean.	4.27	4.01	4.63

TABLE III.—RESULTS OF SUCCESSIVE EXTRACTIONS. TIME, ONE DAY FOR EACH EXTRACTION. GRANDEAU'S METHOD, FOUR PER CENT AMMONIA. PEAT SOIL.

		A. Per cent.	B. Per cent.	Mean. Per cent.	Remarks.
1st extraction, 750 cc....		16.90	18.96	17.93	
2nd " 250 "		2.80	2.38	2.59	
3rd " 250 "		1.77	1.10	1.44	
4th " 250 "		1.34	1.30	1.32	
5th " 250 "		0.89	0.85	0.87	
6th " 250 "		1.41	1.65	1.53	
7th " 250 "		2.10	1.80	1.95	Washed again with HCl for Ca. Trace found. HCl washed out, but trace of chloride found in ash. Probably HCl absorbed from air as humus showed small quantity of a white volatile solid on evaporation.
8th " 250 "		0.67	0.65	0.66	
9th " 250 "		0.57	0.50	0.53	
Total..... 2750 "		28.45	29.19	28.82	

349. Summary of Results.—1. The modified method gives much higher results than the original method of Grandeau.

2. In the Grandeau method marked irregularities follow a change in the strength of the ammonia solution. These differences in results bear no relation to the strength of the solution used. They seem to be errors due to the difficulty of securing uniform and complete washing of the soil by the ammonia solution.

In the modified method the change in the strength of the ammonia solution makes practically no difference in the amount of humus extracted, except in the case of the peat where two per cent ammonia failed to extract all the humus. But the results show no considerable increase when the strength is increased to over four per cent.

3. The factor of time has not been fully investigated, but the results so far obtained indicate that the time exerts less influence in the modified than in the Grandeau method.

4. Table III shows that considerable quantities of the peat soil are still passing into solution in the Grandeau method at the end of ten days. With ordinary soils this is not true; but in the case of soil No. 5, a black soil, the solutions were colored at the end of a week. On the peat soil the modified method extracted from ten

to 50 per cent more than the Grandeau, and on the ordinary soil from two to three times as much humus.

5. In comparing duplicate results by both methods it is found that with soil No. 3 (peat), the following differences appear calculated to percentage of the total amount involved in the determination:

	Per cent.	Per cent.	Per cent.	Per cent.
Strength of ammonia.....	2.0	4.0	7.0	8.0
Modified method.....	1.7	5.0	1.0	1.8
Grandeau method.....	13.0	4.3	0.5	3.4

Special attention was paid to this point in case of No. 7, an ordinary soil; taking all results into consideration the greatest difference in percentage of total amount involved was, by the modified method, 19 per cent, and by the Grandeau, 30 per cent. In the set of six special determinations made by both methods to test this point and which are strictly comparable with each other, the maximum range was by the modified method 7.8 per cent and by the Grandeau 8.3 per cent of the total amount involved in the determination. From which it appears that the modified method is on the whole capable of yielding rather more concordant results than the Grandeau.

350. Official Method of Determining Humus.—The method of humus determination, adopted by the official chemists, is that of Huston and McBryde, with a few minor variations.⁴⁴

Ten grams of the sample are extracted in a gooch with successive small quantities of a one per cent hydrochloric acid solution until the filtrate is shown to be free of lime on testing with ammonia and ammonium oxalate. The excess of acid is removed by washing with water.

The contents of the crucible, including the asbestos felt, are washed into a cylinder marked at 500 cubic centimeters with a four per cent solution of ammonia to the mark, and digested, after closing the mouth of the cylinder with its glass stopper and with frequent shaking for 24 hours. The cylinder is placed in an upright position for 12 hours, the supernatant liquor filtered, and an aliquot part taken for analysis. The sample is evaporated to dry-

⁴⁴ Bulletin 46, Bureau of Chemistry : 76.

ness and weighed after drying at 100°. After ignition the humus is calculated from loss of weight.

351. Estimation of Free Humic Acids.—This process, due to Müntz⁴⁵ is the forerunner of that of Huston and McBride. Twenty grams of the soil are reduced to a fine powder and saturated with 50 cubic centimeters of concentrated ammonia and allowed to digest two or three days in a warm place with frequent shaking. The volume is then made up to one liter with water, well shaken, and set aside for one day in order to permit the subsidence of the solid matter. At the end of this time 500 cubic centimeters of the supernatant liquor are acidified with hydrochloric acid in order to precipitate the humic bodies. The humus is collected on a filter, dried and weighed. It is then ignited and the weight of ash deducted from the first weight thus giving the actual weight of the humus obtained, free from mineral matter. This process gives the free humic acids. By previous treatment of the sample with hydrochloric acid as in the process of Huston and McBride, the total humus is obtained. The estimation of the free humic acids is of importance in determining the quantity of lime or marl which should be added to acid lands.

352. Humus Method of van Bemmelen.⁴⁶—Van Bemmelen obtains the content of humus by the multiplication of the content of carbon in the soil by the factor of Wolff; *viz.*, 1.724. The estimation of carbon, water, and of the loss on ignition is conducted in combustion tubes in a current of oxygen. The nitrogen estimation is carried on according to the method of Dumas.

In soils containing calcium carbonate the organic carbon content is derived from the total carbon dioxid taken up by the potash bulbs during combustion (a); from other carbonates not decomposed on ignition and which are subsequently determined in the residue by treatment with hydrochloric acid in a carbon dioxid apparatus, (b), and the total carbon dioxid derived from the carbonates in the soil (c).

For each estimation from three to five grams of the soil are used, because with smaller quantities the errors of analysis too

⁴⁵ Encyclopédie chimique, 4 : 182.

⁴⁶ Die landwirtschaftlichen Versuchs-Stationen, 1890, 37 : 279 et seq.

strongly influence the results. The carbon is then calculated according to the formula:

$$\text{Carbon} = \frac{1}{11} (a + b - c).$$

The Carbon Dioxid of Carbonates.—It is necessary to expel the carbon dioxid at ordinary temperatures, because on heating to boiling, carbon dioxid would be formed from the humus. In a flask, as small as possible, the soil is treated at ordinary temperature, with dilute sulfuric or citric acid, the escaping gas dried over sulfuric acid, and taken up with soda-lime. Behind the soda-lime is a small tube filled with pieces of glass and moistened with sulfuric acid, which retains any moisture taken out of the soda-lime. A quantity of about one liter of air, free from carbon dioxid slowly drawn through the apparatus is sufficient to drive out all of the carbon dioxid when the estimation is made at ordinary temperatures.

A volcanic earth from Deli, which contained five per cent of humus, gave, at a temperature near 15° , 0.01 per cent CO_2 . At boiling temperature two analyses gave 0.54 and 0.56 CO_2 . This soil contained no carbonate, and the carbon dioxid found at the boiling temperature, must have come from the humus substances under the influence of the dilute acids.

A heavy clay containing 6.9 per cent of humus gave, at near 15° , 3.60 per cent CO_2 ; at 100° without boiling, it gave an additional 0.53 per cent, and with boiling an additional 0.11 per cent, or a total of 4.24 per cent CO_2 . A light clay containing 3.2 per cent of humus, gave, at 15° , 5.09 per cent CO_2 ; at a boiling temperature an additional 0.43 per cent, and by continued boiling an additional 0.27 per cent.

353. Estimation of Humus by the German Method.—The German experiment stations follow the method of Loges,⁴⁷ depending on the oxidation of the humic bodies with copper oxid after evaporation of the sample with phosphoric acid. The object of the preliminary evaporation is to decompose the carbonates and set the humic acids free in order that they may be better and more easily oxidized than when burned in the combined state.

The sample of soil is placed in a Hoffmeister dish (schälchen),

⁴⁷ Die landwirtschaftlichen Versuchs-Stationen, 1883, 28 : 229, and 1891, 38: 311.

moistened with dilute phosphoric acid and evaporated to complete dryness. The dish and its contents are rubbed up with pulverized copper oxid and placed in a combustion tube of 60 centimeters in length, open at both ends. There is then placed in the tube, and held in place by asbestos plugs, granular copper oxid to a length of 20 centimeters.

The combustion tube is placed in a proper furnace and one end connected with two washing-flasks, the first containing potash lye, and the other a solution of barium hydroxid. These flasks are to free the aspirated air from carbon dioxid. The other end of the combustion tube is connected with an appropriate apparatus for absorbing the carbon dioxid. Loges recommends the Pettenkofer absorption tube and a Fresenius drying cylinder.

Between the absorption apparatus and the aspirator, is also placed a washing-flask containing barium hydroxid solution, serving to detect any unabsorbed carbon dioxid. The layer of granular copper oxid is first heated, the air being slowly aspirated through the apparatus meanwhile, but not through the absorption bulbs. All the carbon dioxid is thus removed from the apparatus.

The absorption system being connected, the tube is heated slowly from the front, backwards, and after the tube is well heated a slow current of air is drawn through and continued until the combustion is complete, which is usually in about three-quarters of an hour.

After the tube is cool the powdered copper oxid and residue of combustion are removed, and for this reason the tube is stopped with a cork at both ends instead of being drawn out and sealed at one end. The tube can thus be refilled without disturbing the granular layer of copper oxid.

The drying cylinder used between the combustion tube and the absorption system has its upper part filled with cotton to avoid the deleterious effects of the nitric oxid produced in the combustion. With this arrangement the use of metallic copper in the combustion tube to reduce the nitric oxid can be dispensed with, the moist cotton holding back the acid fumes. The per cent of humus is obtained by multiplying the per cent of carbon found by 1.724.

354. Method of Raulin for the Estimation of Humus.⁴⁸—The

⁴⁸ Comptes rendus, 1890, 110 : 289 et seq.

principle of this method rests upon the very feeble solubility in water of potassium phospho-molybdate and the greater solubility of the phospho-molybdates of sodium, magnesium, calcium, iron, and aluminum. The process does not require complex separations nor a very large quantity of soil. The volumetric estimation of humus in soil by a solution of potassium permanganate would be convenient and practical if the combustion of the organic matter were complete, and if the browning of the liquor did not render the end of the reaction uncertain. The process of Schmidt, modified as below, has given satisfactory results.

In a small flask, with flat bottom, containing about 250 cubic centimeters, are introduced ten cubic centimeters of a solution of manganese sulfate containing 16 grams of the anhydrous salt per liter, and ten cubic centimeters of a ten per cent solution of potassium permanganate. The solution is heated for a few minutes, the liquor is decolorized and manganese bronze (hydrated manganese dioxid) is precipitated. One hundred cubic centimeters of water and four cubic centimeters of sulfuric acid containing 150 cubic centimeters of monohydrated acid per liter are added. There is now added an exactly measured volume of the humic liquid properly prepared, so that in oxidizing completely it destroys at most only half of the manganese dioxid. The mixture is submitted to gentle ebullition for eight hours, the water being kept at a constant volume. The excess of manganese dioxid remaining is dissolved (hot) by a measured portion of decinormal oxalic acid in slight excess, and the excess of oxalic acid is oxidized by a solution of potassium permanganate containing one gram per liter. The volume of oxalic acid not consumed by manganese dioxid is calculated from the amount of permanganate consumed. The volume of oxalic acid, which corresponds to the same quantity of dioxid as the introduced humus, is also calculated by taking the difference between the volume of oxalic acid necessary to destroy all the dioxid formed by ten cubic centimeters of the ten per cent permanganate solution, and the volume of the oxalic acid which has destroyed the dioxid remaining after the action of the humus. The first volume of oxalic acid, that is to say, that which destroys the dioxid formed by ten cubic centimeters of ten per cent permanganate is determined in a preliminary titration.

In regard to the humic liquor, it is prepared by treating ten grams of earth with soda solution in the usual manner. It will be easy to calculate the volume of the oxalic solution equivalent to the total volume of the humic solution, of which a determined fraction has been assayed, and consequently the volume of oxalic solution equivalent to the humus in ten grams of the dry earth. This number of cubic centimeters of the decinormal oxalic solution multiplied by 0.8 will express in milligrams the weight of oxygen necessary to burn the humus from ten grams of dry earth. Humus not being a definite compound, but a residue of complex organic matters partially oxidized, it will require as much more oxygen to complete the combustion as the previous oxidation has been less pronounced. This weight of oxygen necessary to burn the humus from ten grams of dry earth may serve to show the total value as well as the weight of the humus itself. However, if we wish to have directly the weight of the humus, resource can be had to a table which, without being rigorous, can be regarded as sufficiently exact when the variability of the constitution of humus is taken into account.

Volume of decinormal oxalic acid for 10 grams of dry earth. cc.	Corresponding humus, directly determined. mg.	Volume of decinormal oxalic acid for 10 grams of earth. cc.	Corresponding humus directly determined. mg.
50.....	80	1600.....	1560
100.....	150	1800.....	1720
200.....	280	2000.....	1890
300.....	400	2500.....	2315
400.....	510	3000.....	2735
500.....	610	3500.....	3170
600.....	705	4000.....	3605
700.....	790	4500.....	4035
800.....	885	5000.....	4460
900.....	975	5500.....	4890
1000.....	1060	6000.....	5310
1200.....	1225	6500.....	5745
1400.....	1390		

355. Pasturel's Method.—According to Pasturel⁴⁹ the process of Raulin does not furnish figures that are rigorously exact except with soil of which the humus contains 45 per cent of carbon. When the richness in organic carbon is less, the results of the esti-

⁴⁹ Annales agronomiques, 1890, 16 : 558 et seq.

mation are too high. Pasturel modifies the process as follows:

Manganese Sulfate.—Dissolve 16 grams of the pure anhydrous manganese sulfate in distilled water and make the solution up to one liter.

Potassium Permanganate.—Make a solution of ten grams of potassium permanganate in one liter of water; 100 cubic centimeters of the liquor just mentioned are diluted to one liter and constitute the potassium permanganate solution one to ten.

Oxalic and Sulfuric Acids.—A solution of oxalic acid is prepared containing 6.3 grams of the acid in one liter of water, and a dilute solution of sulfuric acid, by dissolving 150 grams of the monohydrated acid in one liter of water.

Humus Solution.—The solution of humus is prepared by the following process: Ten grams of fine earth are freed from all their carbonates by dilute hydrochloric acid. After washing, the filter is broken and the dirt is washed into a small flask. Not more than 20 or 30 cubic centimeters of water should be employed for this purpose. Twenty cubic centimeters of a liquor containing two grams of caustic soda are added, and the flask is placed upon a sand-bath and maintained at a boiling temperature for six hours. It is then diluted with water, filtered and washed as long as the waters are colored. The liquor is treated with dilute sulfuric acid until almost the whole of the soda is saturated. It is indispensable, however, to maintain a slight alkalinity in order that the organic matter may rest totally dissolved. The precipitation of flocculent silica which is almost always produced is without inconvenience. Afterward the volume is completed to 500 cubic centimeters and the humus solution is then ready for use.

Estimation of the Humus.—Ten cubic centimeters of the manganese sulfate are placed in a flask and ten cubic centimeters of the permanganate added, and the whole is then slightly heated, and afterward 100 cubic centimeters of water and four cubic centimeters of sulfuric acid are added. The humic liquor is now introduced in such proportion that the humus which it contains dissolves at the greatest, a half of the precipitated manganese and the rest of the process is continued as described by Raulin.

The principle objection to these two processes is evidently the

manner in which the humus solutions are prepared. The tendency to produce humus bodies on heating organic matter (carbohydrate) with a fixed alkali has already been pointed out. The methods of Raulin and Pasturel, therefore, are not such as promise the most accurate results.

356. The Estimation of Soil Acidity to Determine Quantity of Lime.—Within the past few years, it has been definitely shown that the reaction of a soil exerts a marked influence on its crop-producing power. While the reaction affects the chemical and the physical condition of the soil to a considerable extent, the growth of plants is more directly affected by the action of the acids on the plant roots, and upon the micro-organisms of the soil.

The importance of the matter has led to the elaboration of several methods for determining the amount of acids in soil, but, owing to the exceedingly small amount usually present in ordinary arable soils, the influence of other material, and the constant changes taking place in the soil, none of these methods has shown a close relation between crop production and the amount of acidity as determined by any of the methods.

The usual method of determining whether a soil is acid or not is to press a piece of delicate blue litmus paper against the moistened soil and note the rapidity with which the color is changed to pink. A somewhat more delicate method, particularly with soils which contain practically no free acids but are yet in need of liming, is the following proposed by Veitch:⁵⁰

About ten grams of soil are treated with 100 cubic centimeters of distilled water in a Jena flask and allowed to stand over night. Fifty cubic centimeters of the supernatant liquid are carefully drawn off and boiled with a few drops of phenolphthalein in a covered Jena beaker until the appearance of the pink color, or to a volume of about five cubic centimeters with no development of color. The pink color shows the soil to be alkaline, while no color shows it to be acid or neutral.

Wheeler, Hartwell and Sargent⁵¹ have recently made a critical examination of the methods which have been proposed for this purpose, checking the chemical methods by field experiments.

⁵⁰ Journal American Chemical Society, 1904, 26 : 661.

⁵¹ Journal American Chemical Society, 1900, 22 : 153.

These investigators were unable to correlate the chemical results obtained by any of the methods examined with the field results, but regarded as promising the titration of dilute ammonia which had been in contact with the soil for some time, and also a modification of the method of Tacke based on the evolution and estimation of the carbon dioxide freed from calcium carbonate by the acid soil on boiling them together in water.

357. Method of Tacke.⁵²—This method designed primarily for determining the free acids in moor soils consists essentially in expelling the carbon dioxide from calcium carbonate brought in contact with the soil at ordinary room temperature.

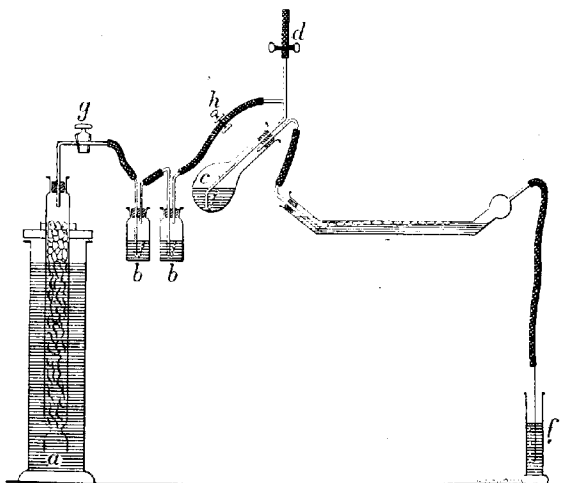


Fig. 77. Tacke's apparatus for free acids in soils.

The apparatus employed by Tacke is illustrated in figure 77. The decomposition flask *c* contains the finely divided fresh peat soil whose acidity is to be determined. The air is removed from *c* by a stream of hydrogen generated in *a*, and washed in *b b*, containing, respectively, acid and alkaline solutions. The hydrogen escaping from *c* passes through a Pettenkofer absorption tube *e*

⁵² Chemiker Zeitung, 1897, 21 : 174.

and enters into the vessel *f* under water. The stream of gas is regulated by the pinch-cock *h* and by lowering or raising the exit tube in *f*. The three way tube entering *c* also carries a pinch-cock *d*, by means of which the carbonate of lime, in the form of suspended silt, can be introduced into *c*. The sample of peat soil, and from 100 to 200 cubic centimeters of water are placed in *c* and the whole system subjected to the action of the hydrogen for about an hour in order to remove any oxygen or carbon dioxide which may be present. For wetting the suspended silt freshly boiled water is employed, and also the liquid for generating the hydrogen must be freshly boiled before using. *e* contains about 100 cubic centimeters of $N/5$ or $N/10$ soda lye. An excess of suspended carbonate of lime is added through *d*, care being taken to admit no air, and the contents of *c* are thoroughly mixed by shaking, and the stream of hydrogen continued for three additional hours. The contents of *e* are brought into a beaker and titrated with $N/5$ or $N/10$ hydrochloric acid, using phenolphthalein as indicator.

Or the liquid is finally removed from the tube, avoiding the absorption of carbon dioxide from the air, barium chlorid added and the solution titrated with $N/5$ or $N/10$ hydrochloric acid using phenolphthalein as an indicator with attention to the points brought out by the investigations by Küster⁵³ and by Lunge⁵⁴.

The acidity of several samples of peaty soils was determined by this method, and found to vary from 1.72 per cent to 2.24 per cent. The practical application of this method would lead at once to the determination of the proper amount of lime which should be added for the neutralization of the acidity in the peaty soil.

For example, a soil which in the circumstances described above, yields 1.70 per cent of carbon dioxide indicates a need of about 4,000 kilos of lime per hectare. The acidity of the peat thus determined has also important bearings on the behavior of the soil with slag and natural phosphates.

Wheeler's modification of this method consists of boiling in water the mixed soil and calcium carbonate and determining the carbon dioxide evolved, but elimination of carbon dioxide continues

⁵³ Zeitschrift für anorganische Chemie, 1896-7, 13 : 127.

⁵⁴ Zeitschrift für angewandte Chemie, 1897, 10 : 3.

indefinitely owing to reactions between the soil constituents and the calcium carbonate. Vietch has found that even an alkaline soil containing calcium carbonate will continue to evolve carbon dioxid when treated in the same manner.

HOPKIN'S METHOD.

This method was proposed at the 19th meeting of the Association of Official Agricultural Chemists⁵⁵ by Hopkins and his associates of the Illinois station. It is based upon the reaction which occurs when solutions of mineral salts are added to an acid soil. The organic acids of the soil are themselves very difficultly soluble, and it is practically impossible to completely extract them from the soil with distilled water, even though large quantities of water be percolated through the soil; but, when a mineral salt solution is added to the soil, the organic acids (humic acid, etc.,) unite with the mineral base, forming neutral humates, etc., and liberating the mineral acid, which, of course, is perfectly soluble, and whose titrating power furnishes a basis for determining the total acidity of the soil. The method consists in shaking 100 grams of soil with 250 cubic centimeters of five per cent sodium chlorid solution for three hours and titrating 125 cubic centimeters of the boiled, clear filtrate with standard alkali, using phenolphthalein as indicator. The result multiplied by four equals the acidity in terms of cubic centimeters of standard alkali required to neutralize 100 grams of soil. The factor four is used in place of the natural factor two, because by repeatedly removing one-half of the clear salt solution, restoring the volume with five per cent salt solution, shaking and titrating as before, it is found that the total alkali required for 100 grams of soil averages approximately four times the first titration.

Veitch⁵⁶ has recently studied the method very thoroughly and finds that there is no setting free of appreciable quantities of hydrochloric acid and that there is practically no reaction between the organic matter and the salt solution, whereby difficultly soluble organic acids are dissolved, but that the acidity of the filtrate (or that acidity which is greater than would be given by water under the same conditions) is due chiefly to the solution of alumina or some other base yielding an acid-salt. It appears that the hydrated

⁵⁵ Bulletin No. 73, Bureau of Chemistry.

⁵⁶ Journal of the American Chemical Society, 1904, 26 : 637.

neutral silicates or aluminates are quite strongly attacked by the salt solution, resulting in the replacement of aluminum by sodium, or a breaking-up of the compound, and the consequent formation of an acid solution of aluminum chlorid, the titration of which, with alkali, constitutes the apparent acidity as determined by this method.

It was found that the ratio between successive filtrates is not a constant one, but varies considerably. Hopkins, *et al.*, found it to vary from 0.62 to 0.8, and Veitch found it to vary from about .6 to 1.

The method is very simple in execution, and for this reason very attractive to the busy chemist. It is not, however, a method which determines the total apparent acidity of a soil, nor can it be said that it determines the acidity injurious to sensitive crops.

By this method an approximate determination of the amount of aluminum or other acid-salt forming bases dissolved by sodium chlorid under the conditions of the method can be secured, and the lime required to neutralize such acid-salts be calculated. But as different salts and different concentrations of the same salts dissolve different quantities of these bases, it can not be assumed from chemical data that lime would act in the same way that normal sodium chlorid does, nor that the action of sodium chlorid is a final measure of the lime requirements of soil.

358. The Lime-Water Method.—This method is a modification of the method of Tacke⁵⁷ and is based on the fact that after the affinity of the soil for calcium as bicarbonate is satisfied, the presence of the slightest amount of this salt is manifest by the pink color produced when phenolphthalein is boiled with a portion of the water which has been in contact with the treated soil.⁵⁸ It is claimed for this method that it represents the maximum lime requirements of a soil.

The method of manipulation is as follows:—

To three portions of soil, each consisting of as many grams as the standard lime-water contains tenths milligram of lime (CaO) per cubic centimeter, add from 50 to 60 cubic centimeters of dis-

⁵⁷ Chemiker Zeitung, 1897, 21 : 174.

⁵⁸ Veitch, Journal of the American Chemical Society, 1904, 26 : 637 et seq.

tilled water and different amounts of standard lime-water. For example, to the first add ten cubic centimeters, to the second 20 cubic centimeters, and to the third 30 cubic centimeters of lime-water. Evaporate on the steam-bath, transfer to stoppered Jena flasks with 100 cubic centimeters of distilled water, allow to stand 15 hours, with occasional shaking, draw off 50 cubic centimeters, place in a Jena beaker, add a few drops of phenolphthalein solution, and boil until the appearance of the pink color, or in case no color is developed, to a volume of about five cubic centimeters. Then with two portions of treated soils, one of which has been rendered alkaline by the lime-water and the other of which is still acid, as guides, prepare three fresh portions of ten grams each and add lime-water as before, except that the amount added to one dish differs from that added to another by one or two cubic centimeters. Dry, take up with 100 cubic centimeters of water, allow to stand, draw off, and treat exactly as before. The smallest amount of lime-water which gives the characteristic pink color is taken as the acidity equivalent of the soil. Each cubic centimeter of standard lime-water is equivalent to an acidity of 0.01 per cent expressed as calcium oxid.

The most serious objection to the method, from the analyst's standpoint, is the number of determinations which must frequently be made before the end point is reached.

In the practice of the lime-water method it has been found that the length of time the treated and dried soil is allowed to stand in contact with water has a considerable effect on the apparent acidity as determined by this method. When the treatment continues from 48 to 72 hours, the pink color with phenolphthalein is developed with less added lime-water than where the solution is allowed to stand 16 hours or less, so that some soils which are acid when allowed to stand 16 hours give an alkaline filtrate when allowed to stand from 24 to 48 hours longer.

These results appear to be due to the slow solubility and hydrolyzation of the neutral lime compounds that are formed with the added lime-water, or to the solution and hydrolyzation of neutral compounds already present in the soil. It has long been believed that the bases of the soil go into solution partly as bicarbon-

"acidity" in soils is very general. Most soils, even those common minerals, particularly the zeolites and feldspars, when reduced to fine powder and treated with carbon dioxide free water, gave a more or less strong reaction with phenolphthalein.

Both of these classes of minerals are believed to be present in most soils, but from the nature of the origin of soils the more soluble forms are not likely to be present in considerable amounts, nor are the more insoluble forms likely to be present in a finely divided state. Hence the solution of such minerals would be expected to be slow and the development of an alkaline reaction on long standing, with smaller amounts of lime-water, might be thus accounted for.

359. Nature of Soil Acidity.—Our knowledge the nature of "acidity" in soils is very general. Most soils, even those which would be reckoned as very acid by any of the various methods which have been proposed for determining soil acidity, contain but little water-soluble acids or acid salts. Practical farm experience has strongly indicated that the acids which may be removed from soils by simple treatment with water are not the total harmful acids which they may contain. It has been assumed that very difficultly soluble organic acids as "humic," "ulmic," etc., and their acid salts, the "humates," "ulmates," etc., are chiefly responsible for the harmful acidity of soils, and it has been the object in devising methods for determining soil acidity to reach such compounds.

Veitch⁵⁹ in a careful comparison of the sodium chlorid method and the lime-water method has shown that such compounds are not the only ones which go to make up soil acidity, that there is no close relation between the "acidity" as determined by either of the methods and the toxicity of such acidity, and concludes that acidity, as determined by these methods, cannot be of the same nature in all soils.

Until we have more definite evidence as to the nature and effect of the various compounds which are reckoned as constituting a part of the total apparent acidity of soils, he suggests tentative-

⁵⁹ American Journal of Science and Arts, 1845, 5 : 5.

⁶⁰ Journal of the American Chemical Society, 1904, 26 : 661.

ly and for purposes of further study the following classification of acidity.

Active or actual acidity, due to relatively soluble organic and inorganic acids and acid salts; and *inactive or negative acidity*, reaching, in some soils actual neutrality, as determined by the usual indicators. This latter condition, constituting a part of the absorptive power of soils, appears to be due to the presence of certain constituents, such as the easily attacked hydrated or colloidal silicates, and many non-acid organic compounds, which have a strong affinity for sodium, potassium, calcium, and magnesium. On solution of these bases by the soil water, or on their addition in alkaline compounds they combine immediately with these practically neutral constituents, which thus prevent the reaction of the soil from becoming alkaline until the above-mentioned affinity is satisfied. This condition, while harmful to sensitive plants, is certainly not so harmful as the condition due to free acids or acid salts. Further than this, the reaction which takes place between certain of these soil constituents and added chlorids, sulfates, etc., produces positively acid salts, as we have seen from the reactions of the sodium chlorid method. There can be but little doubt that it is due partly, at least, to the acidity thus produced that the injury arising from the use of chlorids and ammonium sulfate on acid or neutral soils, is to be ascribed.

If it is true that crops are most profitably produced only when the soil is completely neutralized or faintly alkaline, the separation and estimation of the several components of the total apparent acidity is not of much practical importance. On the other hand, if it is not necessary to completely neutralize the total apparent acidity, it becomes necessary to devise methods for the estimation of the harmful acidity, and determine to what it is due.

As a beginning along this line the water-soluble acids and acid salts may be determined. The negative acidity due to easily attacked silicates may be estimated by means of the sodium chlorid method, using a proper correcting factor. The total apparent acidity may be determined by the lime-water method, and by subtracting the acidity determined by the sodium chlorid method, the acidity due to insoluble organic matter is ascertained.

360. Estimation of Carbonates in Arable Soil.—The principle of the determination depends on the liberation of the carbon dioxide from its compounds in the soil by acting on them with an acid, which is capable of displacing the carbonic acid and the desiccation, absorption, and weighing or measuring the evolved gas. Any of the ordinary forms of apparatus for estimating carbon dioxide may be used in this determination.

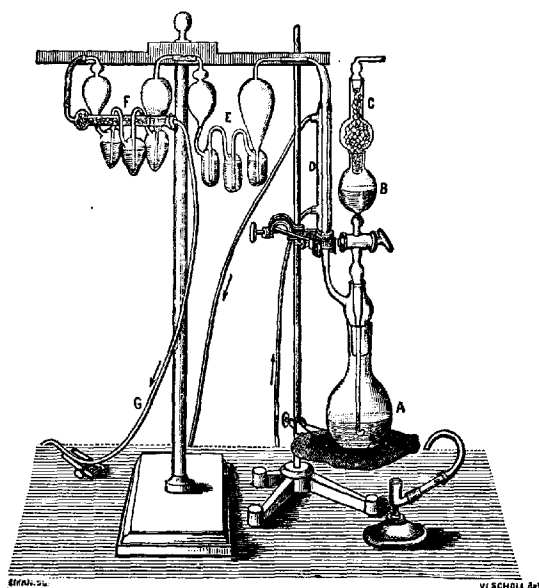


Fig. 78. Knorr's Apparatus for the Determination of Carbon Dioxide.

The apparatus of Knorr⁶¹ has been used with satisfaction for many years in the laboratory of the Department of Agriculture.

The apparatus consists of a flask A, Fig. 78, in which the carbon dioxide in the soil is liberated. A condenser, D, fits by means of a ground-glass joint into the neck of the flask in which the liberated gas, together with any air or aqueous vapor which may be

⁶¹ Bulletin No. 13, Division of Chemistry : 590.

carried forward, is cooled. This prevents any excess of vapor of water from entering the absorbing bulbs, which could easily happen at the end of the experiment when the contents of A are raised to the boiling point. The bulb B contains the acid, usually hydrochloric, which is employed for decomposing the carbonates. It is provided with a guard bulb-tube, C, the contents of which serve to absorb any carbon dioxid which might enter the apparatus with the air during aspiration at the close of the determination. The carbon dioxid is dried in the bulb-tube, E, in oil of vitriol, and absorbed in the potash solution in F. It is advisable to aspirate a slow current of air through the apparatus by means of the tube G during the whole of the operation. The quantity of the sample to be taken depends on its richness in carbonates. Many soils are so poor in carbonates as to render any attempt at exact determination nugatory. On the other hand, a comparatively small sample of marls will be sufficient. A preliminary qualitative test will indicate, in a genral way, the quantity of the sample to be used. The sample of soil, from five to 50 grams, according to its content of carbonates, having been transferred to A, which should be perfectly dry, is made into a batter with freshly boiled distilled water. When all the parts of the apparatus are properly connected gas-tight, the cock between B and A is slowly opened and the hydrochloric (nitric) acid in B allowed to flow into A at such a rate as will secure a moderate evolution of gas.

When the carbonate is entirely decomposed, a lamp is brought under A and its contents gradually raised to the boiling point. The aspiration of air, free from carbon dioxid, is meanwhile continued until all the liberated gas has been absorbed in F. Usually about 15 minutes will be sufficient to accomplish this purpose.

361. Bernard's Calcimeter.—For a rapid and approximately accurate method of determining the amount of carbonate in the soil, estimated as calcium carbonate, Bernard makes use of the well-known method of the volumetric estimation of carbon dioxid. The sample to be examined should not be powdered in any way. The sample in a natural state, well air-dried, is gently broken up by the fingers and passed through a sieve having ten meshes to the centimeter. Of the fine earth thus obtained, one gram is taken for

the determination. If the percentage of carbonate in the soil exceeds 50 then only half a gram is taken.

The apparatus employed is one well known. The small erlenmeyer C is fitted with a rubber stopper carrying an exit tube for the gas and a small thermometer. This flask is connected by means of a rubber tube and small glass tube to the measuring burette B. This burette is graduated from 0 to 100 cubic centimeters. Below, by means of a rubber tube, it is connected with the open bulb, A, which, by means of a cord about its neck, can be suspended by the hook as shown in the figure. The measuring tube is filled with water through A until the level of the liquid in B is slightly above the zero mark. Meanwhile the one gram of earth has been placed in C, together with the tube D three-fourths filled with an equal mixture of water and strong hydrochloric

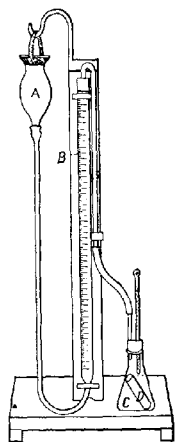


Fig. 79. Bernard's Calcimeter.

acid. The greatest care must be taken that no part of the acid be spilled.

The rubber stopper is now forced into C until the level of the water in B is just at the zero mark. Grasping C in the right hand and A in the left, the operator inclines C until the contents of D

are emptied. Meanwhile as the gas is evolved, A is lowered at such a rate as to always keep the level of the water in B and A on the same plane. In a few moments the evolution of gas is complete, and the volume given off is read at once without correction. This volume multiplied by 0.4 gives the percentage of carbonate in the sample examined. It is understood that the determination is made at ordinary temperatures; *viz.*, 17° to 22°. Example:

The above method is useful in the classification of chalky soils and in determining approximately the quantity of calcium carbonate which they contain. It is of little value in the study of soils containing but little carbonate or compounds of carbonic acid decomposed with difficulty in the cold. Moreover, in the cold a notable quantity of the gas remains dissolved in the dilute acid and is absorbed by the water used in the preliminary moistening of the soil.

362. Soils Deficient in Carbonates.—When a soil contains but a small quantity of carbonates, Müller⁹² has called attention to the fact that the carbon dioxid absorbed by the water in which the soil is rubbed up may vitiate the result. Instead of water a titrated solution of sodium carbonate is employed. The apparatus is composed of a flask containing the mixture of the sodium carbonate and the soil on which the hydrochloric acid is to act. The hydrochloric acid is contained in a small tube, as in the apparatus described above. The gas is received in a rubber tube 1.5 meters long and from three to four millimeters interior diameter, and connected with a burette, the open mouth of which dips into the water of a cylinder of proper length. The volume of gas is read when the burette is raised or lowered in the cylinder until the liquid within and without stands at the same level.

During the action of the acid on the carbonates the flask is constantly shaken.

Several readings of the volume of gas are made, the evolution flask being vigorously shaken before each one. Finally, in order to allow for the variations in temperature and pressure of the ex-

One gram of a sample treated as above, gave of carbon dioxid (uncorrected) 65 cc. $65 \times 0.4 = 26.00$ per cent. calcium carbonate in sample.

⁹² Bulletin de la Société chimique de Paris, 1889, [3], 2 : 483.

terior air which may take place between the beginning and the end of the reaction, a second flask containing air is placed by the side of the evolution flask and communicating with a narrow U-tube half filled with water. Any variations in the volume of the air in the flask will be shown by variations in the height of the liquid in the two arms of the U-tube, and the volume of the variation can be easily determined by having the U-tube calibrated.

If now a equals the volume per cent of carbon dioxide in the atmosphere of the evolution flask at the end of the reaction, v the volume of gas disengaged, and V the volume of the atmosphere in the evolution flask, the per cent of carbon dioxide contained in a given length of the rubber tube will be equal to $\frac{a}{2}$. This arises from the fact that the first gas which passes into the rubber tube is composed solely of air, while the last contains a per cent of carbon dioxide. By reason of the shaking of the flask the mean richness of the contents of the tube in carbon dioxide, will be sensibly $\frac{a}{2}$.

From the above data the following equations are derived:

$$1. \quad v_2 + Va = v.$$

$$2. \quad a = \frac{v}{\frac{v}{2} + V}.$$

If the weight of the carbon dioxide dissolved in V' cubic centimeters of the liquid in the evolution flask be represented by q , the coefficient of the solubility of pure carbon dioxide in this liquid will be, according to the law of the solubility of a gas, equal

$$\text{to } k = \frac{q}{V'a}.$$

The value of k has been determined for various strengths of the sodium carbonate solution, using five cubic centimeters of hydrochloric acid containing 1.6 grams pure hydrochloric acid. For solutions disengaging from five to fifty milligrams of carbon dioxide, the mean value of k is found to be 1.8 milligrams in the absence of calcium chlorid. When calcium chlorid is present in quantities varying from 0.03 to 0.07 gram per cubic centimeter of liquid in the evolution flask, the value of k is 1.4 milligrams.

By adopting, according to circumstances, the one or the other of the above numbers and multiplying it by Va , as determined by experiment, results are obtained differing only 0.2 to 0.3 milligram from those secured by direct weighing of the evolved gas.

Dietrich⁶³ at a much earlier date called attention to the necessity of adding the volume of the dissolved gas to the measured volume in such determinations, and this volume or weight is easily determined by the above formulas.

364. Belgian Method.—The method pursued at the Gembloux Station⁶⁴ consists in rubbing up from five to 50 grams of the sample of soil, according to its contents in carbonate, in a porcelain dish with distilled water in order to make a thin paste. The mass is worked to drive out all the air, the whole washed into a flask of 300 cubic centimeters capacity, and the amount of carbon dioxide estimated by setting free with an acid, and collecting the carbon dioxide evolved in potash bulbs.

DIGESTION OF SOILS WITH SOLVENTS.

365. General Considerations.—There are two points in connection with the determination of mineral matters in the soil which must always be kept in view; *viz.*, first, the estimation of the total quantities of material in the soil, and second, the study of those materials which are more easily brought into solution and thus made available for the food of plants.

It is well understood that the soil particles do not give up entirely to the plant the food materials which they contain. The practical value therefore of an analysis of a soil depends more upon the exact determination of the plant food available than upon its total quantity. From a mineral and geological point of view, on the other hand, an idea of the total composition of the soil is the object to be attained.

For the determination of the available plant food, various solvents have been proposed, none of which, perhaps, imitates very accurately the natural solvent action of organic life and moisture on the soil materials. A description of the standard methods of

⁶³ *Zeitschrift für analytische Chemie*, 1864, 3 : 162 et seq.

⁶⁴ *Petermann, L'Analyse du Sol* : 20.

preparing soil extracts will be the subject of a few succeeding paragraphs. The solvents which have been prepared and used include water, water containing carbon dioxide, solutions of organic acids, solutions of salts of ammonia, mineral acids, hydrofluoric acid and carbonates of the alkalis and other solvents.

366. Estimation of the Quality of Materials Soluble in Water and Other Weak Reagents.⁶⁵—Five hundred grams of the air-dried soil are treated in a flask with 1,500 cubic centimeters of water, less the quantity of water already contained in the air-dried soil which is volatile at 125°. The mass is frequently shaken, and, after 72 hours, 750 cubic centimeters of the liquid filtered. The filtrate is evaporated to dryness in a platinum dish, dried at 120° and weighed. This is then incinerated and, after treatment with ammonium carbonate and gentle ignition, is again weighed. The further examination of the residue for acids and bases is made by some of the methods hereafter described.

Treatment with Water Saturated with Carbon Dioxid.—Two thousand five hundred grams of the air-dried soil are treated with 8,000 cubic centimeters of distilled, and afterwards with 2,000 cubic centimeters of water, which have previously, at room temperature, been saturated with carbon dioxide. The mixture is left in a closed flask for seven days, frequently shaken, after which 7,500 cubic centimeters of the liquid are filtered. The clear filtrate, after treatment with a little hydrochloric acid and a few drops of nitric acid, is evaporated to dryness. After the separation of the silica the traces of iron, alumina, lime, sulfuric acid, magnesia, potash, and soda, are estimated in the liquid in the manner hereinafter to be described. Phosphoric acid is always present in such a case but in such small quantities as to make its estimation a matter of some difficulty.

Treatment with Water Containing Ammonium Chlorid.—In the flask containing the residue from the last experiment; *viz.*, the soil with 2,500 cubic centimeters of liquid, are added 1,500 cubic centimeters of water saturated with carbon dioxide, and 8,000 cubic centimeters of pure water in which five grams of ammonium chlorid are dissolved. The mixture is then left for seven

⁶⁵ Zeitschrift für analytische Chemie, 1864, 3 : 97.

days, with frequent shaking, and 7,500 cubic centimeters of the liquid are then filtered, and the substances dissolved, determined in the filtrate. In addition to the usual quantities of lime and magnesia, from two to four times as much alkali is dissolved by this treatment as is found in the solution from the water containing carbon dioxide alone.

Treatment with Water Containing Acetic Acid.—The acetic acid should be of such a strength that after it has fully acted on the soil it should still contain 20 per cent of free acid. One thousand grams of the soil dried at 100° are used and the acid added in proper proportions and treated in the manner to be described for determining the solvent action of hydrochloric acid.

367. Treatment with Citric Acid Solution.—In ascertaining the quantities of soil materials soluble in a solution of citric acid, Dyer⁹⁶ recommends the use of a solution of one per cent strength. The digestion is carried on as follows: Place in a flask or bottle, holding about three liters, 200 grams of air-dried soil and two liters of distilled water, in which are dissolved 20 grams of pure citric acid. The soil is left, at room temperature, in contact with the one per cent acid for seven days, with thorough shaking several times a day. Each sample is shaken approximately 400 times. At the end of the digestion the solution is filtered and 500 cubic centimeters of the filtrate, corresponding to 50 grams of the soil, are used for analysis for each ingredient to be determined.

The digestion in citric acid is especially recommended by Dyer because of its supposed near resemblance to the methods of solution of plant food in contact with the rootlets of plants. It is evident, however, that this process is in no sense an imitation of natural methods. The solution is used chiefly for the estimation of potash and phosphoric acid. Dyer concludes, from a comparison of the action of a solution of citric acid on soils of known fertility, that when as little as 0.01 per cent of phosphoric acid is dissolved from a soil by this treatment it is justifiable to assume that it stands in immediate need of phosphatic manure. The methods used by Dyer to determine the phosphoric acid and potash in the citric acid solution will be given in their appropriate place.

⁹⁶ Journal of the Chemical Society, Transactions, 1894, 65 : 115.

368. Comparison of Some Common Methods of Extracting Soils with Weak Solvents.—In view of the fact that many methods of extracting from the soil mineral elements which are important to the growth of plants have been proposed, Hall and Plymen have subjected the more common of them to comparative tests.⁶⁷

Of the common methods compared; *viz.*, (a) extraction with a one per cent citric acid solution, (b) with corresponding quantities of hydrochloric and acetic acids, (c) with a saturated solution of carbonic acid, and (d) within an ammoniacal solution of ammonia citrate they recommend as the process giving results most in harmony with field results the method (a).

Ingle has subjected soils extracted with citric acid to pot cultures and shown that such soils have lost the greater part of their fertility.⁶⁸

Attention is called to the fact, however, that changing conditions of temperature, rainfall and sunshine must be taken into consideration in the interpretation of the data obtained.

369. Treatment with Hydrochloric Acid.—The solutions of soils usually subjected to chemical analysis are those obtained by long treatment with hot mineral acids, among which the most common is hydrochloric.

It has long been assumed by soil analysts, perhaps not with justness, that such treatment removed from the soil, all those elements of plant food which could possibly be available for the needs of the growing crop. In this connection, however, the analyst must not forget that nature, in a series of years, with her own methods may easily accomplish what he in five days, even with the help of a hot mineral acid, may not be able to secure. Since, however, this method of solution has been so long practiced it is not the place here to throw doubt on its effectiveness without being able to suggest a better way. Of the mineral acids available no one possesses solvent powers for soils in a higher degree than hydrochloric. A somewhat detailed description will therefore be given of the methods of its use.

370. Strength of Acid to be Employed.—The fact that hydro-

⁶⁷ Journal of the Chemical Society, Transactions, 1902, **81** : 117.

⁶⁸ Journal of the Chemical Society, Transactions, 1905, **87** : 43.

chloric acid of nearly constant strength; *viz.*, specific gravity 1.115, equivalent to 22.9 per cent hydrochloric acid, may be obtained by distillation, led Owen to use acid of this density in his classic work on soil analysis. Hilgard has lately reviewed the conditions of constant strength in the solvent with results confirming the statements of Owen⁶⁹. He evaporated on a steam-bath, to one-half its bulk, 50 cubic centimeters of hydrochloric acid, specific gravity 1.116, obtained by using the distillate from a stronger acid after rejecting the first third. The same operation was conducted with similar acid diluted with 10 per cent of water. The acid used contained 22.96 per cent hydrochloric acid. The residual acid contained 21.49 per cent hydrochloric acid. These results lead Hilgard to believe that the changes arising from evaporation in hydrochloric acid during soil digestion are insignificant, compared with those due to its action on the soluble matters, and that evaporation during digestion is effective in maintaining a definite strength in the solvent. For this reason it is contended that evaporation in a porcelain beaker covered by a watch-glass is more effective in constancy of conditions than digestion in a closed flask under pressure.

371. Influence of Time of Digestion and Strength of Acid.—

Loughridge has made an interesting study of the influence of the strength of acid and time of digestion on the solution of soils.⁷⁰ The method of preparing the soil for the determination of the above points is as follows:

The soil, having been passed through the appropriate number of sieves to obtain the fine earth is pulverized with a wooden pestle and thoroughly mixed. The hygroscopic moisture is determined, after exposing it in a place saturated with vapor, in a layer not exceeding one millimeter in thickness for 12 hours, and subsequently drying at 200° in a paraffin-bath. Of this dried substance from two to three grams are used in the general analysis, the methods employed being in general those adopted by Peter.⁷¹

The quantities of materials dissolved by acids of different densities are shown below. The determinations are made by methods hereafter to be described.

⁶⁹ *Agricultural Science*, 1894, **8** : 1, et seq.

⁷⁰ *American Journal of Science and Arts*, 1874, [3], **7** : 20, et seq.

⁷¹ *Geological Survey in Kentucky*, 1857, **3** : 177 et seq.

Ingredients.	Specific gravity of acid.		
	1.10	1.115	1.160
Insoluble residue	71.88	70.53	74.15
Soluble silica	11.38	12.30	9.42
Potash	0.60	0.63	0.48
Soda	0.13	0.09	0.35
Lime	0.27	0.27	0.23
Magnesia	0.45	0.45	0.45
Manganese oxid	0.06	0.06	0.06
Ferric oxid	5.15	5.11	5.04
Alumina	6.84	8.09	6.22
Sulfuric acid	0.02	0.02	0.02
Volatile matter	3.14	3.14	3.14
Total	99.92	100.69	99.56
Amount of soluble matter	24.00	27.02	22.27
" " " bases	13.50	14.70	12.83

From the above table it is seen that the strongest acid exerts the least soluble effect upon the substances present in the soil, while the greatest degree of solution was obtained by the acid of 1.115 specific gravity. This result indicates that while lime and magnesia are probably present chiefly as carbonates, potash as well as alumina, and to some extent lime, are present as silicates, and for that reason are not as fully extracted by acid of low strength as by that of medium concentration.

In regard to the influence of the time of digestion, the acid of specific gravity 1.115 being used, the data obtained are given in the following table:

Ingredients.	Number of days digested.				
	1.	3.	4.	5.	10.
Insoluble residue	76.97	72.66	71.86	70.53	71.79
Soluble silica	8.60	11.18	11.64	12.30	10.94
Potash	0.35	0.44	0.57	0.63	0.62
Soda	0.06	0.06	0.03	0.09	0.28
Lime	0.26	0.29	0.28	0.27	0.27
Magnesia	0.42	0.44	0.47	0.45	0.44
Manganese oxid	0.04	0.06	0.06	0.06	0.06
Ferric oxid	4.77	5.01	5.43	5.11	4.85
Alumina	5.15	7.38	7.07	7.88	7.16
Phosphoric acid	0.21	0.21
Sulfuric acid	0.02	0.02	0.02	0.02	0.02
Volatile matter	3.14	3.14	3.14	3.14	3.14
Total	99.78	100.68	100.57	100.69	99.78
Amount of soluble matter	19.67	24.88	25.57	27.02	24.85
" " " bases	11.05	13.68	13.91	14.49	13.68

From this table it appears that the amount of dissolved ingredients increases up to the fifth day, the increase becoming, however, very slow as that limit is approached. It is also found that the ingredients offering the greatest resistance to this action are the same as those whose amounts were sensibly affected by the strength of the acid; namely, silica, potash, and alumina.

In regard to lime and magnesia, one day's digestion not being sufficient for full extraction, it is evident that they do not exist in the soil as carbonates or hydrated oxids only, as has been supposed, but also as silicates. A comparison of the results of the five and ten days' digestion shows that the solvent action of the acid has substantially ceased at the end of five days, there being no further increase of the amount of dissolved matter. In fact, some of the silica soluble after five days appears to become insoluble on further digestion.

372. Digestion Vessels.—Hilgard prescribes that the digestion of the sample of soil with acid be conducted in a small porcelain beaker covered with a watch-glass.⁷² Kedzie, however, prefers beakers of bohemian glass, and shows as Fresenius also affirms that hydrochloric acid attacks the porcelain with greater energy than the glass.⁷³ Platinum would be the ideal material for the digestive vessels, but its great cost would exclude its general use for commercial work. In most cases it will be found that the error introduced into the analysis by the use of porcelain or bohemian glass beakers is quite small and not likely to affect the quantitative estimation of valuable soluble soil ingredients to any extent, except soda and potash.

In the laboratory of the Bureau of Chemistry some comparative tests made by Bigelow have shown that vessels of hard glass of special manufacture are less soluble in hot hydrochloric acid of 1.115 specific gravity than porcelain, thus confirming the observation of Kedzie. Following are the data showing the weights of material dissolved in 50 hours:

	Milligrams.
Berlin porcelain.....	2.8
Bohemian glass.....	1.7
Kaehler and Martini glass.....	1.2

⁷² Bulletin 38, Division of Chemistry : 77.

⁷³ Bulletin 38, Division of Chemistry : 83.

In each case 25 cubic centimeters of the acid were used. The vessels all had approximately a capacity of 200 cubic centimeters.

373. Processes Employed.—Hilgard's Method.—The sample of soil sifted through a 0.5 millimeter mesh sieve and thoroughly air-dried, is conveniently preserved in weighing tubes. The actual content of hygroscopic and combined moisture may be previously made on a separate sample of soil.

In determining the amount of material to be employed for the general analysis regard must be had to the nature of the soil. This is necessary because of the impracticability of handling successfully such large precipitates of alumina as would result from the employment of as much as five grams in the case of calcareous clay soils; while in the case of very sandy soils even that quantity might require to be doubled in order to obtain weighable amounts of certain ingredients. For soils in which the insoluble portion ranges from 60 to 80 per cent, from two and a half to three grams is about the right measure for general analysis, while for the phosphoric acid determination not less than three grams should be employed in any case. It has been alleged that larger quantities must be taken for analysis in order to secure concordant results. It is difficult to see why this should be true for soils and not for ores, in which the results affect directly the money value, while in the case of soils the interpretation of results allows much wider limits in the percentages. Correct sampling must be presupposed to make any analysis useful; but with modern balances and methods it is difficult to see why five grams should be employed instead of half that amount, which in some cases is still too much for convenient manipulation of certain precipitates.

The desired quantity, usually from two to two and a half grams is brought into a small porcelain beaker, covered with a watch-glass, treated with from eight to ten times its bulk of hydrochloric acid of 1.115 specific gravity, and two or three drops of nitric acid, and digested for five days over the laboratory steam-bath. At the end of this time it is evaporated to dryness, first on the water-bath and then on the sand-bath. By this treatment all the silica set free is rendered insoluble.

374. Method of the Official Agricultural Chemists.—Place ten grams of the air-dried soil in a 150 to 200 cubic centimeter erlenmeyer flask, add 100 cubic centimeters of pure hydrochloric acid of specific gravity 1.115, insert the stopper with a long condensing tube, place in a steam-bath, and digest for ten hours at the temperature of boiling water, shaking once each hour. Pour the clear liquid into a small beaker, wash the residue out of the flask with distilled water onto a filter, and add the washings to the contents of the beaker. The residue is the amount insoluble in hydrochloric acid. Add a few drops of nitric acid to the filtrate to oxidize organic matter, and evaporate to dryness on the water-bath; take up with hot water and a few cubic centimeters of hydrochloric acid, and again evaporate to complete dryness. Take up as before, filter and wash thoroughly with cold water or with hot water slightly acidified at first with hydrochloric acid. Cool and make up to 500 cubic centimeters. This is solution A. The residue is to be added to the main residue and the whole ignited and weighed as insoluble matter.

Bigelow found in comparison made in the laboratory of the Bureau of Chemistry that digestion in flasks covered only with a watch-glass gives a larger quantity of dissolved matter in five days than the digestion under pressure does in 36 hours. The respective quantities of soluble and insoluble matter obtained by the two methods in two soils are as follows:

Method of digestion.	Soil No. 1. Per cent.		Soil No. 2. Per cent.	
	Insoluble.	Soluble.	Insoluble.	Soluble.
Open flask.....	75.62	24.38	79.62	20.38
Closed flask	76.81	23.19	80.48	19.52

375. Digestion with Continuous Agitation and at Constant Temperature.—The temperature at which a solvent acts on a soil has an important bearing on the quantity of material which passes into solution. The persistence of agitation also affects the progress of solution in a notable way.

An apparatus adapted by the author from Wagner's device for treating phosphatic slags and shown in figure 80 is used.

The apparatus is constructed of galvanized iron and as originally made, has double walls with half inch air space between

them. Where digestions are to be made at temperatures only slightly above that of the laboratory a cheaper form,⁷⁴ devised by Moore, with single walls answers every purpose.

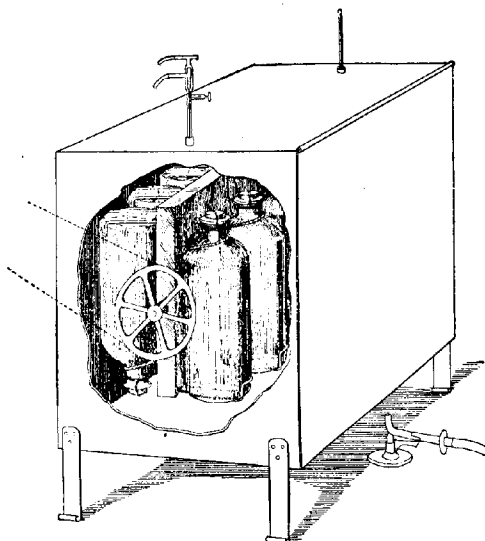


Fig. 80. Shaking Machine for Soil Extraction at Constant Temperature.

In the figure the end of the box is cut away to show the revolving board to which the digestion bottles are attached. These bottles are of about two liters capacity, closed when ready for use by rubber stoppers tied in. A convenient size of digester carries six bottles on each side arranged as shown in the figure. A thermometer at one end registers the temperature and a thermostat at the other controls the flame of the lamp.

By the use of this apparatus it is possible to have a uniform agitation and temperature throughout the work. The machine may be run by any motive power at hand at any convenient speed.

376. Digestion with Two-Hundredth Normal Hydrochloric Acid.

—In order to determine approximately the quantities of potash

⁷⁴ Journal of the American Chemical Society, 1902, 24 : 82.

and phosphoric acid in a soil immediately available for an oat crop Moore has developed a method of treatment with dilute hy-

drochloric acid of $\frac{N}{200}$ strength.⁷⁵

The apparatus described in the foregoing paragraph is used and the temperature is kept constantly at 40°. Several years after this apparatus had been in use in the Bureau of Chemistry Passon independently suggested its use.⁷⁶

In order to determine the relation between crop feeding and the solubility of potash and phosphoric acid in the soils a long series of comparisons extending over several years was conducted. The method of digestion finally adopted requires the hydrochloric acid strength to be two-hundredth normal, after the neutralization of carbonates and basic principles, with constant agitation during a period of five hours.

In order to determine the basicity of the sample a preliminary digestion is conducted as follows: Twenty grams of the sample are digested with 100 cubic centimeters of tenth-normal hydrochloric acid for five hours at 40° with constant shaking, the digested mass brought onto a filter and ten cubic centimeters of the clear filtrate titrated with tenth normal alkali using methyl orange as indicator. If nine cubic centimeters of the alkali solution are required to secure neutrality it is evident that one-tenth of the acid used was required to decompose carbonates and neutralize basic matters in the soil. By means of a simple calculation, therefore, the quantity of x strength of acid necessary to produce a filtrate of a normal strength after digestion is ascertained.

It is convenient in each case to use tenth normal acid for preparing the solutions for all digestions of a less acid strength. In cases where the digestion bottles are made to hold one liter, as in those used in the Bureau of Chemistry, the quantity of dry soil used is conveniently made 186 grams. This quantity of soil of usual density placed in a container marked at one liter and which is filled with acid in the following manner. The quantity of tenth

⁷⁵ Journal of the American Chemical Society, 1902, **24** : 79 et seq.

⁷⁶ Zeitschrift für angewandte Chemie, 1893, **11** : 77, and Die landwirtschaftlichen Versuchs-Stationen, 1901, **55** : 25.

normal hydrochloric acid required to give a filtrate of two-hundredth normal strength after digestion with a given sample of soil is poured into the flask containing the sample and sufficient water added to fill the bottle half full. After thorough shaking the bottle is filled to the mark, stoppered as described and placed in the apparatus designed to secure the digestion with constant agitation at a given temperature. The traces of substances dissolved from the glass are of no consequence in soil analysis, excepting lime and potash. Blank experiments are made to determine the quantities of these bodies dissolved which are usually so small as to be of no consequence for practical purposes.

377. The German Station Method.—The method recommended by the German Stations⁷⁷ is greatly different from that described above both in temperature and time of digestion. To one part of the soil are added two parts by volume of a 25 per cent hydrochloric acid solution, the quantity being increased to correspond to any excess of carbonates. The mixture is left for 48 hours with frequent shaking. As an alternate method, one part of soil is treated with two parts by volume of ten per cent hydrochloric acid, and heated on the water-bath, with frequent shaking, for three hours.

The soluble materials are determined in the filtrate by some of the methods usually employed.

378. The Belgian Method.—The method of making the acid extract of the soil at the Gembloux Station does not differ greatly from some of those already described.⁷⁸

The quantity of air-dried material taken is such that it may weigh exactly 300 grams exclusive of the moisture which it contains. It is dried at 150° for at least six hours. The drying is necessary in order to obtain an extract in hydrochloric acid of exactly 1.18 specific gravity. The dry earth is placed in a flask of two or three liters capacity to which one liter of hydrochloric acid of 1.18 specific gravity is added, being careful to take precautions to prevent frothing if much carbonate be present. The acid is allowed to act for 24 hours, it being frequently shaken

⁷⁷ Die landwirtschaftlichen Versuchs-Stationen, 1891, 38 : 311.

⁷⁸ Petermann, L'Analyse du Sol : 17.

meanwhile. After settling it is decanted and filtered upon a double-folded filter, the apex of which rests upon a small funnel covered with a plain filter of strong paper. Five hundred cubic centimeters of the filtrate are taken for the estimation, and in this filtrate are estimated the silica, phosphoric and sulfuric acids, potash, soda, iron, alumina, lime, and magnesia.

The filtrate is evaporated to dryness in a porcelain capsule, a few drops of nitric acid being added from time to time, and the liquid kept well stirred. The residue should be taken up with water, and if not perfectly free of organic matter, a second and even a third evaporation with nitric acid should take place, until all the organic matter is destroyed, which will be indicated by the clear yellow or reddish-yellow color of the liquid, caused by the iron oxid. After the last evaporation the material is dried in a drying oven one hour at 110° . The changes which take place in the solubility of the constituents of a soil when heated to 150° will be noticed hereafter. By reason of these changes in the soil the method of Petermann is open to grave objections.

379. Treatment with Cold Hydrochloric Acid.—According to the digestion method of Wolff⁷⁹ the soil sample is treated with cold concentrated hydrochloric acid. The process is as follows:

Four hundred and fifty grams of the soil dried at 100° are placed in a glass flask and treated with 1,500 cubic centimeters of hydrochloric acid of 1.15 specific gravity, corresponding to 30 per cent of gaseous hydrochloric acid. For every five per cent of calcium carbonate which the soil may contain, an additional 50 cubic centimeters of hydrochloric acid are added. With frequent stirring, the soil is left in contact with the acid for 48 hours and then 1,000 cubic centimeters of liquid, as clear as possible, are poured off, which corresponds to 300 grams of the soil. After dilution with water it is filtered and the filtrate treated with a few drops of nitric acid and evaporated to dryness to destroy organic matter and render the dissolved silica insoluble. After the separation of the silica the solution is again made up with water to 1,000 cubic centimeters.

Two hundred cubic centimeters of this solution, corresponding

⁷⁹ *Zeitschrift für analytische Chemie*, 8 : 92.

to 60 grams of the soil, are used for the estimation of iron, alumina, lime, manganese, and magnesia.

Four hundred cubic centimeters of the solution, corresponding to 120 grains of the soil, are left for the estimation of sulfuric acid and alkalis. This method gives from five to six times less alkalis and a much smaller quantity of iron than the treatment with hot acid. In the use of hot acid, therefore, Wolff reduces the quantity of soil acted on to 150 grams.

380. Treatment with Nitric Acid.—For the purpose of estimating phosphoric acid Grandeau⁸⁰ directs that the soil be extracted with nitric acid. For this purpose 25 grams of the air-dried fine earth are placed in a porcelain dish covered with a watch-glass, and treated cautiously with nitric acid in small quantities at a time. If the soil be calcareous in its nature it should be previously moistened with water, and the acid so added as to avoid undue effervescence. Sufficient acid is added to strongly saturate the sample and it is then digested on the sand-bath for two hours; or at least until the organic matters are destroyed, which will be indicated by the cessation of evolution of nitrous vapors. The evaporation is carried to dryness, (removing the cover), the residue taken up with water and dilute nitric acid, digested for half an hour, filtered into a 500 cc. flask, and worked up to the mark.

381. Digestion with Hydrofluoric and Sulfuric Acids.—When a complete disintegration of the siliceous substances in soils is desired as in analysis in bulk, the decomposition is easily accomplished by digestion with the above named acids in a platinum dish. The fine earth is saturated with a concentrated aqueous solution of hydrofluoric acid to which a few drops of sulfuric acid are added. It is then digested until nearly dry. If any undecomposed particles remain, the treatment is continued until complete decomposition is secured. The silica is thus all volatilized as hydrofluosilicic acid and the bases pre-existing in the soil are left as sulfates. This method of treatment is especially recommended when it is desired to estimate the whole quantity of any of the soil constituents with the exception of silica. The silica may, however, be determined in the distillate. Instead of using the solution

⁸⁰ *Traité d'Analyse des Matières agricoles*, 3rd edition, 1 : 144.

of hydrofluoric acid, ammonium fluorid may be employed. In this process the sample of earth reduced to an impalpable powder by grinding in an agate mortar is mixed with four or five times its weight of the ammonium fluorid in a platinum dish and thoroughly moistened with sulfuric acid and allowed to stand at room temperature for several hours. It is then gently heated until all fumes of hydrofluosilicic acid have been driven off, but is not raised to a red heat. If any undecomposed particles remain, the above treatment is repeated.

382. Summary.—In the various methods which have been described for the treatment of soils with solvents it is evident that in most cases the processes are conventional. It is only when complete solution is secured, as for instance with hydrofluoric acid, that definite results are reached. Next in order of definiteness is the process recommended by Hilgard where the data show in so far as they have been tabulated and compared, that evaporation in an unconfined space with hydrochloric acid of 1.115 specific gravity establishes a permanent state of acid strength and reaches at about the temperature of boiling water, a definite degree of solution in about five days. If a continuous agitation should be practiced with this method, as is the case with the digestion process with dilute hydrochloric acid as secured in Moore's method, the time of reaching equilibrium might be materially shortened.

In all the cases where the solvent is a weak mineral acid, an organic acid, carbonic acid, salts or water, it is evident that no condition of equilibrium can be secured within the time ordinarily at the disposition of practical analysts. With such solvents time, temperature and continuity of agitation are dominant factors, which are to be carefully considered when concordant results are to be obtained. The important influence of these factors is fully set forth in the data from the Bureau of Chemistry already cited. The strength of the acid employed and the influence of basic substances and carbonates in diminishing the strength of the solvent have also been pointed out.

For practical purposes and for the sake of comparison the official method of securing the ingredients in a soil soluble in a reasonable time in hot hydrochloric acid is recommended. In this

case, since the degree of solution is not definite the terms of the convention should be rigidly adhered to by all analysts using the process. The data secured by this process, as well as those obtained by Hilgard's, represent the total plant food, with the exception of nitrogen, in a soil which is likely to become available in a large number of years. On the contrary, the data secured by the action of weak solvents at comparatively low temperature represent more nearly the quantities of plant food which the crops of the immediate future shall find at their disposal. Finally the total content of the plant foods in the soil, with the exception of nitrogen, is revealed by the solution of the whole mineral mass, composed as it is chiefly of silica in some form of hydrofluoric acid.

DETERMINATION OF THE QUANTITY AND CHARACTER OF DISSOLVED MATTER.

383. Substances in Solution.—By treatment with solvents as indicated in the preceding paragraphs, greater or less quantities of the original constituents of soil are brought into solution. The total quantity of dissolved matters is determined by drying and weighing the insoluble residue and the percentages of soluble and insoluble matters should be noted; and each portion saved for further examination. In this country the common practice of soil analysis is to digest the sample with hydrochloric acid. The following paragraphs, therefore, will be devoted to the general methods of determining the matters dissolved by that treatment, leaving for later consideration the special methods of analysis. The fundamental principle on which the treatment with hydrochloric acid rests is based on the belief that such treatment practically extracts from the soil all those elements which are likely to become, immediately or in the near future, available for plant food.

384. Hilgard's Methods.⁸¹—(1) *Removal of Soluble Silica.*—The acid filtrate obtained by the process given in paragraph 373 is employed for the following determinations. After the solution obtained has been evaporated to dryness to render silica insoluble, it is moistened with strong hydrochloric acid and two or three drops of nitric acid. The mass is warmed, and after allowing to

⁸¹ Bulletin 38, Division of Chemistry : 77.

stand for a few hours on a steam-bath is taken up with distilled water. After clearing, it is filtered from the insoluble residue, which is strongly ignited and weighed. If the filtrate should be turbid the insoluble residue which has gone through the filter can be recovered in the iron and alumina determination.

The insoluble residue is next boiled for 15 or 20 minutes in a concentrated solution of sodium carbonate, to which a few drops of caustic lye should then be added to prevent reprecipitation of the dissolved silica. The solution must be filtered hot. The difference between the weight of the total residue and that of undissolved sand and mineral powder is recorded as soluble silica, being the aggregate of that set free by the acid treatment and that previously existing in the soil. The latter, however, rarely reaches five per cent.

(2) *Destruction of Organic Matter.*—The acid filtrate from the total insoluble residue is evaporated to a convenient bulk. In case the filtrate should indicate by its color, the presence of any organic matter, it should be oxidized by aqua regia, otherwise there will be difficulty in separating alumina.

(3) *Precipitation of Iron and Alumina.*—The filtrate thus prepared is now brought to boiling and treated sparingly with ammonia, whereby iron and alumina are precipitated, together with any phosphoric acid which may be present if not in excess of quantity necessary to combine with the two bases mentioned. It is kept boiling until the excess of ammonia is driven off, and then filtered hot. (Filtrate A). The previous addition of ammonium chlorid is usually unnecessary. If the boiling is continued too long, filtration becomes very difficult and a part of the precipitate may redissolve in washing. Filtration may be begun as soon as the nose fails to note the presence of free ammonia; test paper is too delicate. Failure to boil long enough involves the contamination of the iron-alumina precipitate with lime and manganese.

(4) *Estimation of Iron and Alumina.*—The iron and alumina precipitate with filter of (3) is dissolved in a mixture of about five cubic centimeters of hydrochloric acid and 20 cubic centimeters of water, filtered and made up to 150 cubic centimeters.

In 50 cubic centimeters determine the iron and alumina together by precipitation with ammonia, after oxidizing the organic matter (in the filter from 3) with aqua regia. Fifty cubic centimeters of the solution are used for iron alone and 50 cubic centimeters are kept in reserve. Determine the iron by means of a standard solution of potassium permanganate after reduction, which is accomplished by evaporating the 50 cubic centimeters almost to dryness with strong sulfuric acid, adding water and transferring the solution to a flask, and then reducing by means of pure metallic zinc in the usual way. The alumina and phosphoric acid are then calculated by difference and the latter determined as described further on deducted to get the weight of alumina. This method of determining the two oxids in their intermixture is in several respects more satisfactory than the separation with caustic alkalies, which, however, has served for most determinations made, until within the last ten years. It is, however, much more liable to miscarry in unpracticed hands than the other.

(5) *Estimation of Lime.*—The filtrate A from the iron and alumina is acidified slightly with hydrochloric acid, and if too bulky is evaporated to about 25 cubic centimeters, unless the soil is a very calcareous one, and the lime is precipitated from it by neutralizing with ammonia and adding ammonium oxalate. The precipitation of the lime should be done in the hot solution, as the precipitate settles much more easily. It is allowed to stand for 12 hours, then filtered (filtrate B), washed with cold water, and dried. By ignition the lime precipitate is partially converted into the oxid. It is then heated with excess of powdered ammonium carbonate, moistened with water, and exposed to a gentle heat (50° - 80°) until all the ammonia is expelled. It is then dried below red heat and weighed as calcium carbonate. When the amount of lime is at all considerable, the treatment with ammonium carbonate must be repeated till a constant weight is obtained.

(6) *Estimation of Sulfuric Acid.*—The filtrate B from the calcium oxalate is put into a hard bohemia flask, boiled down over the sand-bath, and the ammoniacal salts destroyed with aqua regia. From the flask it is removed to a small beaker and evaporated to dryness with excess of nitric acid. This process usually

occupies from four to five hours. The residue should be crystalline-granular. If it is white-opaque, ammonium nitrate remains and must be destroyed by hydrochloric acid. The dry residue is moistened with nitric acid, and the floccules of silica usually present separated by filtration from the filtrate, which should not amount to more than 10 or 15 cubic centimeters. The sulfuric acid is precipitated by treatment with a few drops of barium nitrate, both the solution and the reagent being heated to boiling. If the quantity of sulfuric acid is large it may be filtered after the lapse of four or five hours (filtrate C), if very small it should stand 12 hours before filtering. The precipitate is washed with boiling water, dried, ignited, and weighed. Care should be taken in adding the barium nitrate to use only the least possible excess, because in such a small concentrated acid solution the excess of barium nitrate may crystallize and will not again readily dissolve in hot water. Care must also be taken not to leave in the beaker the large heavy crystals of barium sulfate, of which a few sometimes constitute the entire precipitate, rarely exceeding a few milligrams. Should the ignited precipitate show an alkaline reaction on moistening with water, it must be treated with a drop of hydrochloric acid, refiltered and weighed. The use of barium acetate involves unnecessary trouble in this determination.

(7) *Estimation of Sodium and Potassium*.—Filtrate C is now evaporated to dryness in a platinum dish, the residue is treated with an excess of crystallized oxalic acid, moistened with water, and exposed to gentle heat. It is then strongly ignited to change the oxalates to carbonates. This treatment with oxalic acid must be made in a vessel which can be kept well covered, otherwise there is danger of loss through spattering. As little water as possible should be used, as otherwise loss from evolution of carbon dioxide is difficult to avoid. Spatters on the cover should not be washed back into the basin until after the excess of oxalic acid has been volatilized. The ignited mass should have a slightly blackish tinge which shows the conversion of the nitrates into carbonates. White portions may be locally retreated with oxalic acid. The ignited mass is treated with a small amount of water, which dissolves the alkaline carbonates and leaves the magnesium carbonate, manganese protoxyd, and the excess of barium carbon-

ate behind. The alkalis are separated by filtration into a small platinum dish (filtrate D), and the residue is well but sparingly washed with water on a small filter. When the filtrate exceeds ten cubic centimeters it may, on evaporation, show so much turbidity from dissolved earthy carbonates as to render refiltration on a small filter necessary, since otherwise the soda percentage will be found too large and magnesia too small. If, on dissolving the ignited mass, the solution should appear greenish from the formation of alkaline manganates, add a few drops of alcohol to reduce the manganese to insoluble dioxid.

The filtrate D, which should not be more than 10 or 15 cubic centimeters, containing the carbonates of the alkalis, is evaporated to dryness and gently fused, so as to render insoluble any magnesium carbonate that may have gone through; then redissolved and filtered into a small weighed platinum dish containing a few drops of dilute hydrochloric acid, to change the carbonates into chlorids, evaporated to dryness, and exposed to a gradually rising temperature (below red heat), by which the chlorids are thoroughly dried and freed from moisture, so as to prevent the decrepitation that would otherwise occur on ignition. Holding the platinum basin firmly by forceps grasping the clean edge, pass it carefully over a very low bunsen flame, so as to cause, successively, every portion of the scaly or powdery residue to collapse, without fully fusing. There is thus no loss from volatilization, and no difficulty in obtaining an accurate, constant weight. The weighed chlorids are washed by means of a little water into a small beaker or porcelain dish, treated with a sufficient quantity of platinum chlorid, and evaporated to dryness over the water-bath. The dried residue is treated with a mixture of three parts absolute alcohol and one part ether, which does not dissolve the potassium platinochlorid. This is brought on a filter, and washed with ether-alcohol. When dry, the precipitate and filter are put into a small platinum crucible and exposed to a heat sufficiently intense to reduce the platinum chlorid to metallic platinum and to volatilize the greater part of the potassium chlorid. This is easily accomplished in a small crucible, which is roughened by being constantly used for the same purpose (and no other), the spongy metal causing a ready evolution of the gases. The reduced plat-

inum is now first washed in the crucible with hot acidulated water, then with pure water, then all moisture is driven off and it is weighed. From the weight of the platinum, is calculated the potassium chlorid and the oxid corresponding; the difference between the weights of the total alkaline chlorids and potassium chlorid gives the sodium chlorid, from which may be calculated the sodium oxid. When the heating of the platinum precipitate has not been sufficient in time or intensity, instead of being in a solid spongy mass of the color of the crucible itself, small black particles of metallic platinum will obstinately float on the surface of the water in the crucible, and it becomes difficult to wash without loss.

(8) *Estimation of Manganese.*—The residue of barium, magnesium, and manganese compounds is treated on the filter with hydrochloric acid, and the platinum dish is washed with warm nitric acid (not hydrochloric, for the platinum dish may be attacked by chlorin from the manganese oxid) dissolving any small traces of precipitate that may have been left behind. The solution containing the magnesium and manganese chlorids is freed from barium salts by hot precipitation with sulfuric acid, and the barium sulfate, after settling a few hours, is separated by filtration. The filtrate is neutralized with ammonia, any resulting small precipitate (of iron) is filtered, and the manganese precipitated with ammonium sulfid, let stand 12 hours, filtered (filtrate E); washed with cold water, dried, ignited, and weighed as manganese protosquioxid, Mn_3O_4 . If preferred the manganese may be precipitated with chlorin or bromin water as dioxid, but the process requires a rather longer time and may fail in inexpert hands more readily than the method given.

(9) *Estimation of Magnesium.*—The filtrate E, from the manganese is now freed from sulfur by acidulating with hydrochloric acid, evaporating, if necessary, and filtering. From the filtrate the magnesia is precipitated by adding an equal bulk of ammonia water and then sodium phosphate. After standing at least 24 hours, the magnesium salt may be filtered, washed with ammoniacal water, dried, ignited, and weighed as magnesium pyrophosphate.

385. Examination of Acid Extract by the Methods of Petermann.

—*Estimation of the Silica.*—The Gembloux method of estimating silica consists in taking up the dry extract obtained from the treatment of the soil, in the manner described in paragraph 378, with water and a few drops of hydrochloric acid, heating for a short time on a sand-bath to facilitate the solution, and filtering, washing, drying, igniting, and weighing the residue obtained as silica.

—*Estimation of the Sulfuric Acid.*—The filtrate obtained in the estimation of silica is heated for half an hour with a few drops of nitric acid and the volume made up to 500 cubic centimeters. One hundred cubic centimeters of this are precipitated with barium chlorid, diluted to double its volume, heated for some time, the precipitate of barium sulfate collected and weighed, and the quantity of sulfuric acid calculated therefrom.

—*Potash and Soda.*—Potash and soda are estimated by heating the filtrate obtained in the estimation of the sulfuric acid and precipitating the excess of barium in the hot solution after the addition of ammonia by ammonium oxalate and carbonate. The whole is allowed to digest for six hours at a gentle heat and then allowed to remain at rest for 24 hours, filtered, washed, and the filtrate evaporated to dryness in a large platinum dish and the ammoniacal salts driven off at a low temperature. At the end the temperature is carried a little higher until it reaches low redness. The residue is taken up by distilled water, filtered into a weighed platinum dish, a few drops of hydrochloric acid added, evaporated, dried, heated with great care and the sodium and potassium chlorids obtained weighed together. The respective quantities of potash and soda are estimated in the usual way by precipitating the potash with platinum chlorid, and deducting the weight of potassium obtained as chlorid from the total weight of the double chlorids.

—*Estimation of the Iron and Aluminum Oxids.*—The iron and aluminum oxids are estimated in 25 cubic centimeters of the primitive solution obtained with hydrochloric acid after removal of soluble silica by adding ammonium carbonate almost to complete neutralization, that is to say until the pre-

precipitate formed is just redissolved in the feeble excess of hydrochloric acid which remains, and the liquid changes from a clear red to a blood red tint. Dilute with distilled water and precipitate with a little excess of ammonium acetate, and boil until, after interrupting the boiling for a moment, the basic iron and aluminum acetate and the small quantity of iron and aluminum phosphate present are easily deposited, and the supernatant liquid is limpid and colorless. Wash the precipitate by decantation, boiling each time, filter, wash the filter with boiling water to which a little ammonium acetate has been added, dry, ignite, and weigh. The material obtained consists of ferric oxid, aluminum oxid, and iron and aluminum phosphates. Deduct from the whole, the phosphoric acid determined in another portion. The residue will be the sum of the iron and aluminum oxids.

Estimation of the Lime.—The filtrate from the portion used for the estimation of the iron and alumina, which has a feeble reaction due to acetic acid, is treated hot with ammonium oxalate. The mixture is kept at a gentle heat for at least twelve hours, after which it is filtered, washed with hot water, dried, and ignited over a blast-lamp to constant weight and weighed as calcium oxid.

Estimation of the Magnesia.—For the estimation of the magnesia the filtrate obtained in the estimation of lime is evaporated to dryness in a platinum dish, the ammoniacal salts driven off, the residue taken up with water slightly acidified with hydrochloric acid, filtered, the filtrate made strongly alkaline with ammonia and heated some time to the boiling point to precipitate any traces of iron and alumina which may have remained in solution. Filter, wash, allow to cool and precipitate the magnesia with constant shaking or stirring by the addition of sodium phosphate, allow to stand for 12 hours, collect on a filter, ignite, and weigh as pyrophosphate, and calculate the quantity of magnesia from the weight of salt obtained.

Estimation of the Phosphoric Acid.—The phosphoric acid is estimated in 100 cubic centimeters of the original solution obtained by the treatment of the soil with hydrochloric acid by removing the silica and again evaporating it to dryness on the water-bath. The residue is taken up with water to which a few

drops of nitric acid have been added and filtered. The total phosphoric acid is then obtained by precipitation with ammonium molybdate in the usual way.

386. Analysis of the Insoluble Residue.—The insoluble residue left after digestion with hydrochloric acid is not without interest from an agricultural and analytical point of view. While it is true that the plant food, therein contained, is not immediately available, yet it must not be forgotten that the method of the chemist may not fix a limit to nature's method of collecting nutriment for plants. In however refractory a state they may exist, it is possible that all nutritive elements therein may eventually become available for assimilation. For the completion of an estimate of the total nutritive power of a soil, therefore a further examination of the insoluble residue should be made. The methods of securing this are essentially those of making a bulk analysis of the soil.

The principle of the method depends on the reduction of the sample to an impalpable powder and the subsequent decomposition of the insoluble portions by treatment with hydrofluoric and sulfuric acids or by fusion with the alkalis.

387. Method of Wolff for Treating Residue Insoluble in Hot Hydrochloric Acid.⁸²—The well-washed residue is dried with the filter, then separated therefrom, the filter burned and the ash weighed with the whole of the residue. About eight grams of the residue are ignited and serve for the estimation of the insoluble mineral matter. Another portion of ten grams of the dried, but not ignited, residue is boiled with a concentrated solution of sodium carbonate with the addition of caustic soda, and the quantity of dissolved silicic acid estimated. A third portion of about 15 grams is treated with about five times its weight of pure concentrated sulfuric acid, and is evaporated until the mass has taken the form of a dry powder. After moistening with concentrated hydrochloric acid the mass is boiled with water, filtered, and the filtrate examined according to the ordinary methods for silicic acid, alumina, iron, lime, magnesia, and alkalis. The residue after treatment with concentrated sulfuric acid is dried, but not

⁸² *Zeitschrift für analytische Chemie*, 1864, 3 : 98.

ignited, and boiled with a concentrated solution of sodium carbonate with the addition of a little caustic soda, filtered, heated, and the silicic acid separated from the solution. After thorough washing, the residue, after ignition, is weighed and represents the material insoluble in concentrated hydrochloric and sulfuric acids. The silicic acid found as before, together with the small quantity dissolved in the hydrochloric acid extract, gives, in connection with the alumina contained in the sulfuric acid extract, approximately the quantity of pure water-free clay contained in the soil.

In six samples of soils of very different compositions which were examined by the above process, it was found that the clay had the following mean composition: Silicic acid, 55.1 to 61.5 per cent, alumina, 38.6 to 44.9 per cent; as means 58.05 per cent silicic acid and 41.95 per cent alumina.

Finally, four or five grams of the residue, after treatment with sulfuric acid and sodium carbonate, are rubbed up in an agate mortar and completely separated into silt by water. The silt mass is dried, lightly ignited, and three grams of it spread in a flat platinum dish moistened with sulfuric acid, and subjected to the action of hydrofluoric acid in a lead oven at 60°, until a complete decomposition of the material is accomplished. In the solution all the different bases can be determined.

388. Method of the Belgian Chemists.—The method employed by Petermann⁸³ at the Gembloux Station in the examination of the part of the soil insoluble in hydrochloric acid consists in washing the insoluble portion by decantation with distilled water until all acid reaction is removed. Place the contents of the flask and of the filter in a porcelain dish and dry. After a careful mixing of the mass take out about 50 grams and wash upon a filter until all reaction for chlorin has disappeared, dry, detach the mass from the filter and incinerate. Place in a platinum crucible two grams of the ground and ignited residue and mix it, using a platinum stirring rod, with 12 grams of ammonium fluorid; heat slightly over a Bunsen burner in a muffle with a good draught and regulate the flame in such a way that the operation shall con-

⁸³ I. Analyse du Sol : 21.

tinue for about one hour. After complete decomposition add about two cubic centimeters of sulfuric acid in such a way as to completely saturate the residue, drive off the sulfuric acid carefully at a low red heat and take up the residue with water slightly acidulated with hydrochloric acid and wash the whole into a flask of 500 cubic centimeters capacity. Oxidize by heating for an hour with nitric acid, make up to the mark and filter. The percentages of potash, soda, lime, magnesia, and the silicates are determined exactly as in the hydrochloric acid extract. The decomposition of the silicates by ammonium fluorid has been compared by Petermann with the other standard methods of attack, *viz.*: by a solution of hydrofluoric acid, by the gaseous acid and by fusion with alkaline carbonates, and is preferred by him to all other methods. Some of these methods of decomposition require as much as three days time and introduce into the mass large quantities of substances, such as potash and soda, of which small quantities only exist in the sample to be analyzed. In many hundreds of analyses he has not found in any case that more than two hours were necessary to secure a complete decomposition of the sample with ammonium fluorid.

389. Bulk Analysis.—It is frequently desirable to determine the total composition of a soil sample as well as the nature of that part of it soluble in any of the solvents usually employed. To this end the methods of mineral analysis are employed. The variations which occur in duplicate analyses are probably due to the small quantities of material taken for analysis, it being difficult to obtain average samples of a material which is not very finely powdered when small quantities are used. Moreover, as it is likely to become of importance to know whether the proportions of lime and magnesia vary by as much as one-tenth per cent, and such small variations are within the limits of error of an analysis, and as the total proportion of lime and magnesia in highly siliceous soils, probably does not exceed one-tenth per cent, it is deemed best to take a large quantity of soil for the bulk analysis in each case. The amount adopted for the highly siliceous soils containing much quartz is ten grams. This quantity, taken after quartering down the entire sample, is ground to an

impalpable powder and used for the determination of the lime, magnesia, and alkalies, the silica, iron oxid, alumina, and loss on ignition, being determined in one gram samples. The ten grams are decomposed by hydrofluoric and sulfuric acids or by ammonium fluorid in a large platinum dish, the solution evaporated, at first on the water-bath until all water is removed, and then at a higher temperature until all the free sulfuric acid is driven off, when the residue is heated in a muffle at a low red heat for several hours. At this temperature the sulfuric acid combined with the iron oxid and alumina is driven off, leaving the remaining sulfates unchanged and the iron oxid and alumina are in the form of a powder of no great volume which is easily and quickly washed. This operation is usually successful at first but in some cases the decomposition is not complete as is shown by the appearance of a precipitate on adding ammonia to the filtrate from the aluminum and iron oxids. In such cases the precipitate is dissolved in hydrochloric acid, reprecipitated by ammonia and removed by filtration. In the filtrate from the thoroughly washed aluminum and iron oxids, lime is precipitated as oxalate and separated by filtration; the filtrate is evaporated to dryness and the ammonia salts driven off by heat; the magnesia in the unfiltered watery extract of this residue is precipitated by baryta water, which also removes the sulfuric acid with which the bases had been combined. In the filtrate from this precipitate baryta is precipitated by ammonium carbonate and removed by filtration, leaving the alkalies to be determined in the usual way after conversion into chlorids. The mixed precipitate of magnesia and barium sulfate is treated with hydrochloric acid, filtered, the baryta present removed as sulfate, and the magnesia precipitated in the filtrate from the latter as phosphate. The advantages of this method are that the large quantity of material employed gives some assurance that an average sample has been operated on, and all the bases present in small proportions are estimated in the same sample. The objection to it is the time consumed both in grinding the samples and in determining all the bases in one solution. As a small quantity of material is generally used for determining the silica, iron oxid, alumina, and loss by ignition, and a larger quantity for the remaining bases, slight differences in the unground sam-

ples are unavoidable, especially when the quartz grains are somewhat large, it being practically impossible to take two small samples of such a soil which would have the same number of quartz grains. Consequently tedious grinding of large quantities of the soils for the bulk analysis is necessary. This objection does not apply to the official analysis or assay of soils in which considerable quantities are extracted by acid and the solution analyzed, and silica is not determined. In any case, it may be said, when it becomes an object to know whether a soil contains a total of 0.1 or 0.2 per cent of lime or magnesia, of 0.7 or 0.5 per cent of potash, one analysis even of the large quantity of ten grams would be insufficient to decide the point, and at least the mean of two determinations should be taken. The phosphoric acid may be determined as described further on.

The details of modern methods of mineral analysis are fully described by Hillebrand.⁸⁴

SPECIAL METHODS OF DETERMINATION OF SOIL CONSTITUENTS.

390. Preliminary Considerations.—In the foregoing paragraphs the general outline of the chemical methods of soil examination have been given. There are often occasions, however, which demand a special study of some particular soil constituent. It has been thought proper, therefore, to add here some of the best approved methods of special determinations which have been approved in this and other countries.

In the main, the final determination of any particular element of the soil, and its previous separation from accompanying elements, are based on the general processes already given. The variations in many instances, however, are of such importance as to require special mention.

391. Condition of Potash in Soils.—Potash exists in the soil in very different states. That part of it which is combined with the humus material, or with the hydrated silicates, is easily set free from its combinations and is to be regarded as the more assimilable portion.

The potash in the soil is found chiefly in combination with

⁸⁴ United States Geological Survey, Bulletin No. 176.

silicates, and particularly with the hydrated aluminum silicates, forming clay. As the particles with which it is combined are found in a state of greater or less fineness, the potash itself is set free under the influences of the agents which are active in the soil, with greater or less rapidity, passing into a form in which it can be utilized by plants. In silicates which are very finely divided, such as clay, the potash becomes active in a relatively short time, while in the débris of rocks in a less advanced state of decomposition it may rest for an indefinite period in an inert state. The estimation of the potash which is assimilable in the clay is more important for agricultural purposes than to determine that which may be present in the soil in firmer combination. Treating the sample of soil with water, especially if for a short time, does not furnish any reliable information in regard to the potash which the soil contains, nor of its agricultural relations. Indeed, the absorbing properties of the soil tend to prevent the elimination of the potash in this way, to a certain extent, even when it is found in the soluble state. It is therefore, necessary to employ some stronger solvent to set the potash free, but variable results are obtained, according to the employment of acids, or other active solvents of greater or less concentration and for longer or shorter periods of contact.

392. French Official Methods for Potash.—In the method of the French agricultural chemists⁸⁵, 20 grams of the earth are placed in a dish with a flat bottom, 11 centimeters in diameter, and rubbed up with from 20 to 30 cubic centimeters of water. There is added carefully, and in small quantities, some nitric acid of 36° Baumé until all effervescence has ceased, the mass meanwhile being thoroughly stirred. When the carbonates have been decomposed, which can be told by the cessation of the effervescence, 20 cubic centimeters more of the same acid are added. The dish is heated on the sand-bath for five hours, regulating the heating in such a way that there still remains some acid at the end of the operation and the mass is not thoroughly dry. The acid mass is then taken up with hot water, filtered, and washed with hot water until the amount of filtrate is about 300 cubic centimeters. The filtrate should be received in a flask of about one liter capac-

⁸⁵ *Annales de la Science agronomique*, 1891, 8 : 278.

ity. The filtrate will contain the dissolved potash, soda, magnesia, lime, iron and aluminum oxids, and traces of sulfuric and phosphoric acids. For the elimination of the other substances, with the exception of potash, soda, and magnesia, a few drops of barium nitrate are added, afterwards sufficient ammonia to render the solution alkaline, and finally an excess of ammonium carbonate in powder added in small portions. These materials are added successively and the whole is left to stand for 24 hours. By this operation the sulfuric acid is separated in the form of barium sulfate; the iron and aluminum oxids are precipitated, carrying down with them the phosphoric acid, and the lime is thrown down in the form of carbonate. The mass is filtered and washed several times with hot water. The filtrate contains in addition to potash, soda, magnesia, and the ammoniacal salts which have been introduced. The ammonium salts are destroyed by adding aqua regia and evaporating the liquid to a very small volume. The mass is evaporated in a porcelain dish of about seven centimeters diameter, with a flat bottom, and an excess of perchloric acid added. The evaporation is carried to dryness on a sand-bath, and the heating prolonged until the last white fumes of perchloric acid are disengaged. The mass is left to cool. There are added five cubic centimeters of alcohol, of 90° strength. The mass is triturated by a stirring rod, the extremity of which is flattened, in such a manner as to reduce it all to an impalpable powder. It is left to settle and the supernatant liquid is decanted upon a small filter. The treatment with alcohol of the kind, quantity, and strength described, is continued four or five times. Afterwards, as there may still remain a trace of the sodium and magnesium perchlorates in the interior of the crystals of potassium perchlorate, there are added to the capsule in which all of the alkaline residue has been collected, two or three cubic centimeters of water, and it is evaporated again to dryness and taken up twice with small quantities of alcohol. There are thus removed any traces of sodium and magnesium perchlorates which may have been occluded in the potassium perchlorate crystals. By means of a jet of boiling water the stirring rod and the filter, which contains the small quantities of potassium perchlorate, are washed, and the liquid passing through is received in the capsule

which contains the larger part of the salt. It is evaporated to dryness and weighed.

When there is very little magnesia present, as is generally the case, the estimation of the potash is made without any difficulty by the process just mentioned, but when the proportion of magnesia is high it is found useful to separate it before the transformation into perchlorates. The magnesia is separated by carbonating the residue as indicated in the method for the estimation of magnesia, by treatment with oxalic acid and ignition. By extracting the carbonates of the alkalies thus formed with very small quantities of water, and filtering, they are obtained free from magnesia.

It is advisable to test the purity of the potassium perchlorate formed which sometimes contains a little silica. For this purpose it is dissolved in boiling water, and any residue which remains is weighed, and that weight deducted from the total weight of perchlorate. By multiplying the weight of potassium perchlorate found by the coefficient 0.339, the quantity of potash contained in the 20 grams of soil submitted to analysis is obtained.

Estimation of the Potash Soluble in Cold, Dilute Acids.—(Method of Schlösing). Introduce 100 grams of the soil into a one or one and a half liter flask with from 600 to 800 cubic centimeters of water. A little nitric acid, of 30° Baumé, is added until the carbonate is decomposed and a slight acid reaction is obtained. Afterwards five cubic centimeters of the same acid are added and it is left to digest for six hours, shaking every 15 minutes. Instead of taking the whole of the wash-water for the examination, it is better to extract only a portion of it and so dispense with washing. This process is conducted in the following manner:

The weight P of the full flask having been determined, as much as possible of the solution, is decanted by means of a very small siphon, of which the flow is moderated by fixing a rubber tube with a pinch-cock to its lower extremity. After the decantation is complete, the flask is again weighed, giving the weight of P' ; the weight of liquid taken, therefore, is equal to $P - P'$. To determine the total weight of the liquid, throw upon a filter the earthy residue insoluble in the acid, and after washing and drying it determine its weight r . The weight of the empty dry flask p

is also determined. The total weight of the soil will be, therefore, $P - r - p$. The part of the liquid which was extracted from the flask, and upon which the analytical operation is to be conducted is represented by the formula

$$\frac{P - P'}{P - r - p}.$$

This method avoids washing and evaporation which would be of very long duration. It rests upon the supposition that the solid matter from which the liquor is separated has no affinity for the dissolved substances, and that the total of these substances has passed into the liquor, and that the solution is homogeneous.

In the liquor first decanted as described before, the potash is to be estimated. This liquor contains in addition to potash, soda, lime, magnesia, iron and aluminum oxids, as well as phosphoric, sulfuric, and hydrochloric acids. There is first added to it a little barium chlorid to precipitate the sulfuric acid. It is heated to about 40° in a glass flask and some ammonium carbonate added in a solution containing an excess of ammonium hydroxid. By this process the lime, and the excess of baryta are precipitated in the form of carbonates, the alumina and iron as oxids, and the phosphoric acid in combination with the last two bases. The magnesium carbonate is not precipitated because it is soluble in the ammonium carbonate with which it forms a double salt.

The employment of a gentle heat favors the formation of the precipitate of calcium carbonate in a granular form which lends itself easily to filtration. The contents of the flask are thrown upon a filter and the insoluble residue washed. The filtrate contains the potash, soda, magnesia, ammonia, and nitric and hydrochloric acids. It is concentrated as rapidly as possible by heating in a flask, and afterwards the ammoniacal salts are destroyed by weak aqua regia and the whole is then transferred to a porcelain dish and evaporated to dryness. There is thus obtained a mixture of potassium, sodium, and magnesium nitrates, from which the potash is separated by means of perchloric acid in the manner already described.

Estimation of the Total Potash.—Beside the potash which can be dissolved by the boiling concentrated acids the soil contains

potash combined with silicates, which becomes useful for plant life with extreme slowness. It is often of great interest to estimate the total potash contained in a soil, that is to say, the reserve for the future. In this case it is necessary to free entirely this base from its combinations by means of hydrofluoric acid. The operation is conducted upon two grams of soil previously ignited and reduced to an impalpable powder. The decomposition is conducted in a platinum capsule by sprinkling the sample with a few cubic centimeters of hydrofluoric acid, or solution of ammonium fluorid, and adding a few drops of sulfuric acid. The mass is evaporated to dryness and dissolved in boiling hydrochloric acid. The part which remains insoluble is treated a second time by hydrofluoric and sulfuric and afterwards by hydrochloric acid. All of the potash is thus finally brought into solution. The estimation of the potash, after having obtained it in a soluble state, is conducted in the manner previously described.

Estimation of the Potash as Platinochlorid.—Instead of estimating the potash as perchlorate it can also be transformed into platinochlorid. This process gives as good results as the preceding one, but it is necessary in all cases, to separate the magnesia. After having treated the soil as indicated in the case of the estimation of the potash as perchlorate, the separation of the sulfuric and phosphoric acids, of alumina and iron, of magnesia, and the destruction of the ammoniacal salts in the manner already described, there are finally left the alkalies potash and soda in the form of carbonates. These are transformed into chlorids by adding hydrochloric acid; afterwards they are evaporated to dryness and the mixture of the two chlorids weighed in order to determine what quantity of platinum chlorid it is necessary to add, in order that it be in excess. The quantity of chlorid to be added is calculated so as to be in sufficient quantity to saturate the whole of the chlorids weighed, whether they may be composed wholly of sodium or potassium. In this way there is a certainty of having an excess of platinum. The solution of platinum chlorid used should contain in 100 cubic centimeters 17 grams of platinum. Each cubic centimeter of this solution will be sufficient for a decigram of the sodium and potassium double chlorids. After the

addition of the platinum chlorid the mixture is evaporated in a capsule with a flat bottom, on a water-bath. It is important that the temperature should not exceed 100° . If the temperature should go above this there would be a tendency to form some platinum subchlorids insoluble in alcohol.

The evaporation is continued until the contents of the dish are in a pasty condition and form a rather solid mass on cooling. It is necessary to avoid a complete desiccation. After cooling, the residue is taken up by alcohol of 95° strength. It is allowed to digest with alcohol of this strength for some time, after having been thoroughly mixed and shaken therewith in order to obtain a complete precipitation of the potassium platinochlorid. This digestion should take place under a small bell-jar resting upon a piece of ground glass. The evaporation of the alcohol is thus prevented. The mass is washed by means of alcohol of the same strength and the liquors decanted upon a small filter placed within another filter of identical weight, which serves as a tare for it on the balance. The washing is prolonged until the filtrate becomes colorless. All of the particles in the dish should be brought upon the filter by means of a hair-brush. The filters are now dried at a temperature not exceeding 95° and the platinochlorid received upon the interior filter is weighed. The precipitate may also be washed from the small filter into the capsule in which it was formed by means of a jet of alcohol. The alcohol is evaporated and the precipitate weighed in the capsule. The weighing should be made rapidly on account of the hygroscopicity of the material. The weight obtained multiplied by 0.193 gives the corresponding quantity of potash in the soil.

Purification of the Oxalic Acid.—The commercial oxalic acid used in separating the magnesia, often contains lime, magnesia, and potash. When this reagent is used in a sufficiently large quantity in the estimation of the above substances, it is indispensable to free it entirely from them. This is secured by submitting the oxalic acid to successive recrystallizations. The mother waters are thrown away. After two or three successive crystallizations the traces of potash and magnesia have disappeared and the oxalic acid obtained after ignition leaves no trace of residue.

The purification may also be secured in the following manner:

At a temperature of 60° a saturated solution of oxalic acid is made, the liquid decanted, carried to the boiling point and filtered. Five per cent of nitric acid is added and it is allowed to cool. The crystals which are deposited are collected upon a funnel in which a plug of cotton has been placed, and are washed with a little cold water.

Purity of the Ammonium Carbonate.—The ammonium carbonate employed should not leave any residue whatever on volatilization. In general, it may be said of all the reagents employed in analyses and especially of those employed in large quantities, that it is indispensable to be sure that they contain no traces of the substances which are to be estimated. The acids, ammonia, etc., should always be examined with this point in view.

Estimation of the Soda.—It is often of interest to estimate the soda in the soil, not that it is an element of any great fertility but rather because it is hurtful when in excess. It is always present in the solution prepared for the estimation of potash and is easily estimated by difference. The weight of the mixture of sodium and potassium chlorids being known when the potash is determined, the weight of its chlorids is to be deducted from the weight of the two chlorids and thus the indirect weight of the sodium chlorid is obtained.

A better way is to make a direct estimation. The soda is found entirely dissolved in the alcoholic solution obtained by washing the potash salt as before described, for the separation of the potassium platinochlorid. This alcoholic liquor is evaporated to dryness on a water-bath, in a bohemian flask of about 100 cubic centimeters capacity. The residue obtained consists of sodium platinochlorid and a little platinum chlorid. There is fitted to the bohemian flask a cork stopper carrying two tubes. The apparatus is placed upon a water-bath and kept at about 100° . Through the tube which reaches to the bottom of the bohemian flask, a current of pure hydrogen is passed. The hydrogen passes off through the second tube. The hydrogen completely reduces the salts of platinum. In order that the decomposition may go on more rapidly a few drops of water are added. When the whole mass in the flask has become black owing to the separation of the platinum, it is shaken, evaporated to dryness and hydrogen passed

through a second time. This operation is repeated three or four times, being stopped when the water no longer shows a yellow color. There is then in the flask only a mixture of reduced platinum and sodium chlorid. No trace of sodium chlorid has been lost because the temperature has never exceeded 100° . The sodium chlorid is dissolved by washing with water and filtered. The liquor, which must be absolutely colorless, is evaporated to dryness in a platinum capsule and weighed. There is thus obtained the weight of the sodium chlorid. For verification, the sum of the weight of potassium chlorid calculated from the platinochlorid and the weight of the sodium chlorid should be equal to the initial weight of the mixture of the two chlorids.

393. Potash Methods of the German Experiment Stations.⁸⁶—*a.* To one volume of air-dried fine earth which is obtained by sifting through a three-millimeter sieve, two volumes of 25 per cent hydrochloric acid are added, or more if the soil contains much carbonate. The acid is allowed to act with frequent stirring for 48 hours at room temperature.

b. To one volume of the soil, as above prepared, are added two volumes of hydrochloric acid and the mixture allowed to stand for three hours with frequent shaking, at the temperature of boiling water.

c. (Halle method). One hundred grams of the fine earth are treated with 500 cubic centimeters of 40 per cent hydrochloric acid, made up to one liter with water and allowed to stand for 48 hours with frequent shaking. After filtering the acid extracts above described, a large aliquot part of the filtrate is evaporated for the estimation of the potash. The evaporated residue is washed into a half-liter flask in which the sulfuric acid is precipitated with barium hydroxid, the flask filled to the mark and an aliquot part of the filtrate in a half-liter flask, treated with ammonium carbonate, filtered, and the potash estimated as platinochlorid by the usual method.

394. Method of Raulin for the Estimation of Potash in Soils.⁸⁷—The process rests upon the very feeble solubility in water of po-

⁸⁶ Die landwirtschaftlichen Versuchs-Stationen, 1891, 38 : 311.

⁸⁷ Comptes rendus, 1890, 110 : 289.

tassium phosphomolybdate, while sodium, magnesium, calcium, iron, and aluminum phosphomolybdates are more or less soluble. The process does not require complicated separation and permits of the treatment of a small quantity of soil. The weight of the phosphomolybdate obtained is equivalent to 19 times that of the potash.

The reagent is prepared by dissolving 100 grams of pure crystallized ammonium molybdate in as little water as possible and adding six and a half grams of neutral crystallized ammonium phosphate dissolved in a little water. Aqua regia is added and some ammonium phosphomolybdate is precipitated. The mixture is heated, adding a little aqua regia from time to time, until the solution of the precipitate is accomplished. The whole is then evaporated to dryness, the final temperature of evaporation not being carried above 70°. Four hundred cubic centimeters of water are added and five cubic centimeters of nitric acid, and the contents of the dish heated and filtered. The reagent is then ready for use.

The liquid to be used for washing the potassium phosphomolybdate is prepared by dissolving 20 grams of sodium nitrate in one liter of water, two cubic centimeters of pure nitric acid, and a mixture of about 20 cubic centimeters of the phosphomolybdic reagent and one and a half cubic centimeters of a solution of potassium nitrate containing 80 grams per liter, slightly heated in order to saturate the liquid with potassium phosphomolybdate. The mixture is shaken, allowed to rest, and the liquid part decanted.

For the preparation of the solution in which the potash is to be estimated, a sample of soil of such magnitude as to contain about 15 milligrams of anhydrous potash is used. The potash salts are dissolved by the usual processes and are separated from the largest part of the calcium, iron, and aluminum salts, and converted into nitrates. The solution is reduced to a volume of a few cubic centimeters and slightly acidulated with nitric acid. Four cubic centimeters of the phosphomolybdic reagent are added for every ten milligrams of anhydrous potash supposed to be present. The mixture is evaporated to dryness at 50° and immediately brought upon a very small weighed double filter, with 60 cubic centimeters

of the washing liquor mentioned above. A similar tared double filter is likewise washed with the same liquid at 50° and weighed. The weight of phosphomolybdate multiplied by 0.052 gives the anhydrous potash. This method for a direct precipitation of the potash salts does not have the merits of the perchlorate process and both are inferior in accuracy to the usual platinochlorid procedure.

395. Russian Method for Estimating Potash in Soils.⁸⁸—Ten grams of the air-dried, non-ignited soil are digested with 100 cubic centimeters of ten per cent hydrochloric acid on a steam-bath for 24 hours with frequent shaking. After adding five cubic centimeters of nitric acid to the filtrate it is evaporated to dryness, taken up with dilute hydrochloric acid, filtered, the filtrate saturated with ammonia, the excess of ammonia driven off, again filtered, and the lime separated by ammonium oxalate.

The filtrate is treated with a little barium chlorid for the removal of sulfuric acid and afterwards with ammonium carbonate in excess, and left for 24 hours. After filtering, the solution is evaporated in a platinum dish, the excess of ammonia driven off, the residue taken up with water, filtered, treated with hydrochloric acid, evaporated to dryness, and ignited at low heat. The residue is dissolved in water, filtered, and the potash precipitated with platinum chlorid and estimated in the usual way.

396. Potash Method of the Italian Stations.⁸⁹—The potash in the soil is determined in three forms; *viz.*,

1. Assimilable potash.
2. Potash soluble in concentrated acid.
3. Total potash.

For determination of the first, 100 grams of soil are put into a retort holding a liter and digested with dilute nitric acid.

For the analysis, an aliquot portion of the clear liquid is measured or weighed, and the determination of the potash is made by the common methods.

For an alternate method, from 20 to 50 grams of soil are put

⁸⁸ Thoms, *Zur Wertschätzung der Ackerde*, Second Contribution Riga, 1893, 120.

⁸⁹ *Le Staioni Sperimentali Agrarie Italiane*, 16 : 679.

into a retort of 500 cubic centimeters, moistened with water, and nitric acid is gradually added. After one or two hours there are added from 200 to 300 cubic centimeters of water; the liquid is poured without filtering into a retort and the residue washed by decantation.

In the liquid, after the elimination of the other substances with barium chlorid, ammonium carbonate, etc., the potash is determined by the ordinary methods.

In the second case, by using warm concentrated acids, a portion of the insoluble silica is decomposed, but this decomposition is always partial and the quantity of the potash extracted depends upon the temperature, upon the concentration, upon the duration of the action, and upon the nature of the acid.

The method of moistening from 20 to 50 grams of the soil with water and adding concentrated nitric acid of 1.20 density, in such a manner that the soil shall be completely saturated, may also be employed. Then the temperature is kept at 100° during two hours. In the solution, the potash is determined as usual.

In the third case the soil is decomposed by hydrofluoric and sulfuric acids, or by fusion with alkaline carbonates, and the total potash determined by one of the standard methods.

If it is desired to adopt a general method for the determination of the potash the following points must be carefully considered:

1. The quantity of the soil to be examined.
2. The state of humidity or dryness of the same.
3. The quantity, nature, and concentration of the acid.
4. The quantity of the water.
5. The duration of the treatment.

397. Method of J. Lawrence Smith for Potash.—This method, designed especially for mineral analysis, has been fully approved by the general experience of analysts.

The principle of the method⁹⁰ depends upon the decomposition of silicates on ignition with calcium carbonate and ammonium chlorid. The object of this mixture is to bring into contact with the mineral, caustic lime and chlorid of lime in a nascent state at a red heat, the caustic lime being soluble to some extent in calcium

⁹⁰ Crookes, *Select Methods in Chemical Analysis*, 3rd edition, 1894 : 26.

chlorid at a high temperature. Pure calcium carbonate, made by precipitation of marble, should be used.

The ammonium chlorid should be prepared from crystals of pure, sublimed sal ammoniac, by dissolving in water, and filtering and evaporating the solution until small crystals are deposited, the solution being well-stirred until one-half or two-thirds of the whole has crystallized. The mother-liquor is poured off while still hot, and the crystals dried on an asbestos filter at ordinary room temperature.

A special platinum crucible should be used in the Smith method, but the common crucible, especially if very deep, can be employed. The special crucible is of about double the usual length. Smith recommends a crucible 95 millimeters in length, diameter at top 22 millimeters, at bottom 16 millimeters, and weighing from 35 to 40 grams. The object of the long crucible is to have the part of the bottom containing the silicate subjected to a high heat, while the top of the crucible is at a much lower temperature, thus preventing the loss of alkalis by volatilization.

Method of Analysis.—The samples of soil or silicate containing the alkalis are well pulverized in an agate mortar, and from one-half to one gram of the finely pulverized material used for analysis. This is carefully mixed with the same weight of finely powdered sal ammoniac and the mineral and sal ammoniac rubbed well together in a mortar. Eight parts by weight of calcium carbonate are added in three or four portions, and the whole intimately mixed after each addition. The contents of the mortar are emptied on a piece of glazed paper and then introduced into the crucible, which is tapped gently upon the table until the contents are well settled. It is fixed in the furnace which is used for heating, and a small Bunsen burner is placed beneath the crucible, and the heat applied just about at the top of the mixture and gradually carried toward the lower part until the sal ammoniac is completely decomposed, which requires from four to five minutes. A greater heat is then applied by means of a blast-lamp and the crucible kept at a bright redness for from 40 to 60 minutes. The crucible is allowed to cool, the contents detached and placed in a platinum or porcelain dish of about 150 cubic centimeters capacity, and from 60 to 80 cubic centimeters of distilled water

added. The solution of the flux may be hastened by heating the water to the boiling point. The crucible and its cover are also well washed with hot water until all matter adhering to them is dissolved. After the slaking of the mass it is best to continue the digestion with hot water for six or eight hours, although this is not absolutely necessary. The contents of the crucible are filtered and washed well with about 200 cubic centimeters of water. The filtrate contains in solution all the alkalies of the mineral, or soil, together with calcium chlorid and caustic lime. A solution of pure ammonium carbonate containing about one and one-half grams of the pure salt is added to the filtrate. This precipitates the lime as carbonate. This dish containing the material is placed on a water-bath and its contents evaporated to about 40 cubic centimeters. Two additional drops of ammonium carbonate are added, and a few drops of caustic ammonia, to precipitate any lime which may be redissolved by the action of the ammonium chlorid solution on the calcium carbonate. The contents of the dish are brought onto a small filter and washed with as little water as possible and the filtrate received in a small beaker. The filtrate contains all the alkalies as chlorids, together with a little ammonium chlorid. A drop of ammonium carbonate solution is added to ensure the precipitation of all the lime. If no more lime be present evaporate on a water-bath in a deep platinum dish, in which the alkalies are to be weighed. The dish should have from 30 to 60 cubic centimeters capacity, and during the evaporation should never be more than two-thirds filled. After the evaporation has been completed the dish is slowly heated and then gently ignited over a gas-flame to drive off any ammonium chlorid which may be present. During this process the platinum dish may be covered with a thin piece of platinum to prevent any possible loss by the spitting of the salt after the ammonium chlorid has been driven off. The heat should be gradually increased until it is brought to a point a little below redness, leaving the cover off. The platinum dish is again covered, and when sufficiently cooled placed on a balance and weighed.

If lithium chlorid be present it is necessary to weigh it quickly as the salt being very deliquescent takes up moisture rapidly. The alkalies may now be separated in the usual way.

If the sample under examination contains magnesia the residue in the capsule should be dissolved in a little water and sufficient pure lime-water added to render the solution alkaline. It should then be boiled and filtered. The magnesia will, in this way, be completely separated from the alkalis. The solution which has passed through the filter is treated with ammonium carbonate in the manner first described, and the process continued and completed as above mentioned.

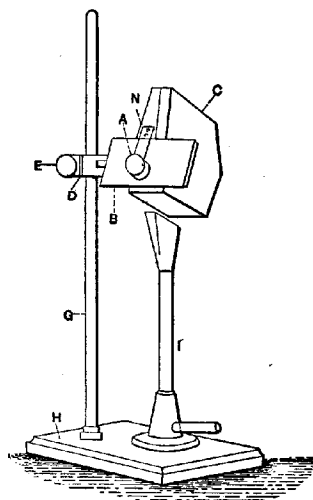


Fig. 81. Smith's Muffle for Decomposition of Silicates.

If it be suspected that the whole of the alkalis have not been obtained by the first fusion, the residue upon the filter can be rubbed up in a mortar with an amount of ammonium chlorid equal to one-half the weight of the mineral, mixed with fresh portions of calcium carbonate and treated exactly as in the first instance. Any trace of alkali remaining from the first fusion is thus recovered in the second one.

Method of Heating the Crucible.—The apparatus used by Smith for igniting the crucible is shown in Fig. 81. It consists

of an iron filter-stand HG, a clamp, ED, carrying the muffle NC, attached by the supports AB, and heated by the lamp F. The muffle NC is a chimney of sheet iron, from eight to nine centimeters long, ten centimeters high, the width at the bottom being about four centimeters on one side and three centimeters on the other. It is made with the sides straight for about four centimeters and then inclined toward the top so as to leave the opening at the top about one centimeter in width. A piece is cut out of the front of the chimney of the width of the diameter of the hole in the iron support and about four centimeters in length, being semi-circular at the top, fitting over the platinum crucible. Just above this part of the chimney is riveted a piece of sheet iron in the form of a flattened hook, N, which holds the chimney in place by being slipped over the top of the crucible support; it serves as a protection to the crucible against the cooling effects of the currents of air.

398. International Method for Assimilable and Total Potash.—

In the International Congress of Chemists held in Paris in 1889,⁹¹ the discrimination between the assimilable and total potash was declared to be of prime importance. Unfortunately no method is known by which the potash which is present in the soil in a state suited to the wants of plants can be determined with entire accuracy. In general, that portion which is given up to weak acids may be assumed to be available. In the treatment of soils with weak acid, as pointed out in the Congress, it is demonstrable that with a 0.05 to 0.1 per cent nitric acid solution, the quantity of potash which goes into solution increases by continued stirring of the mixture with the time of action of the acid up to a certain maximum which is reached in from three to four hours, and after that, it is not changed even when the strength of the acid mixture is increased to two per cent. From this time on, concentrated acids withdraw from the soil which has already been exhausted by the weak acid, a new quantity of potash. The soils which have been exhausted by concentrated acids yield also an additional quantity of potash when they are treated with hydrofluoric acid, or melted with baryta or sodium carbonate. Potash, therefore, appears to exist in the soil in various forms.

⁹¹ Chemiker Zeitung, 1889, 18 : 1391.

First. In the form of undecomposable silicates which have, agriculturally perhaps, very little interest.

Second. In the form of silicates which are more basic than those just mentioned. These silicates are attacked by strong acids and give up probably every year a portion of their potash to vegetation.

Third. In a form which is easily soluble in weak acids and consequently directly assimilable by plants.

In view of the fact that it would be of interest to chemists and agronomists to establish certain methods of investigation so as to be able to obtain comparative results, it was decided to adopt the original method recommended by Gasparin for the estimation of the potash decomposable by concentrated acids. This method consists in the treatment of the soil with boiling aqua regia until the sand which is not decomposed, is white.

Determination of the Fineness of the Earth which is Used for Analysis.—For the estimation of potash, the soil should be divided as finely as possible, and passed through a sieve of 30 meshes to the centimeter. The decomposition is then completed in two hours, while if a sieve of only ten perforations per centimeter is used, the acid must be allowed to work for 12 hours.

The determination of the potash after solution, is accomplished by any of the standard methods.

399. Method of Tatlock as Used by Dyer.—Attention was called in paragraph 367 to the estimation of the total plant food in the soil by extraction of the sample with citric acid. Dyer first determines the total potash by Tatlock's method which is as follows:

To determine potash, ten grams of fine dry soil are treated with ten cubic centimeters of hydrochloric acid and evaporated to dryness on the water-bath, the residue taken up with another ten cubic centimeters of acid, warmed, diluted with water, boiled, filtered, and washed. The filtrate and washings are concentrated and gently incinerated to get rid of organic matter, and the residue redissolved in hydrochloric acid, and evaporated slowly with a considerable quantity of platinum chlorid. If the evaporation be conducted slowly, the potassium platinochlorid settles out well, despite the iron, aluminum, and calcium salts, and is easily washed with some more platinum chlorid solution, followed by alcohol.

The application of this modification of the platinum chlorid process to solutions containing comparatively minute quantities of potash in a great excess of iron, aluminum, and calcium salts is probably new to many chemists. It works admirably, and obviates the necessity for removing iron, aluminum, calcium, magnesium, etc., with the necessary use of ammonia, and the tedious processes of concentration and final volatilization of the ammonium salts; but, of course, the process cannot be employed if soda also is to be determined.

The potash, soluble in hydrochloric acid, having been thus determined, the undissolved siliceous matter is incinerated, weighed, and finely ground in an agate mortar. A weighed portion of it is then, as in the Smith method, mixed with a large bulk of pure calcium carbonate and a little ammonium chlorid and heated, beginning with a low temperature, rising slowly to bright redness. The mass is then boiled with water, washed, incinerated, re-ground, mixed with some more ammonium chlorid, and again heated, boiled, and washed. The process is repeated and the filtrates from all the treatments concentrated, the calcium being removed as carbonate, and the potash determined in the filtrate, after evaporation and incineration at a low temperature, by means of platinum chlorid.

When it is desired to extract the soluble matters with a dilute organic acid 500 cubic centimeters of the citric acid solution of the soil, made as described in paragraph 367, corresponding to 50 grams of soil, are evaporated to dryness in a platinum dish and ignited at a low temperature. The residue is dissolved in hydrochloric acid, filtered, and washed, and the filtrate again evaporated to dryness and treated again as just described. The potash is then determined as above.

400. Moore's Method of Estimating Potash.—In the various methods of determining potash which have been described, except that of Tatlock, it is seen that preliminary to the final process the various bodies with which the potash is associated, such as lime, alumina, iron, titanium, phosphoric acid, etc., must first be removed. The principle underlying Tatlock's and Moore's methods is based on the possibility of securing the content of potash without this troublesome separation. The conduct of the Moore method is as follows:²²

²² *Journal of the American Chemical Society*, 1898, 20 : 342.

The material under examination is brought into solution in acid, ammonium salts, and organic matter destroyed with aqua regia and the excess of acid removed by several evaporations to dryness, care being taken to break up all nitrates with hydrochloric acid. The residue is taken up with water and a few drops of hydrochloric acid, filtered and washed thoroughly. To the filtrate a slight excess of chlorplatinic acid solution is added and evaporated on the steam-bath nearly to dryness so that the salts solidify on cooling. It is important that the evaporation be not carried to complete dryness as the dry iron and aluminum chlorides are exceedingly difficult to dissolve in acidified alcohol. To the cooled mass add from 15 to 25 cubic centimeters of acidified 90 per cent alcohol, stir, and let stand several minutes, filter, wash with alcohol and ammonium chlorid solution and dry in the usual manner. Dissolve the potassium chlorplatinat in hot water, evaporate, dry in water oven for one-half hour, and weigh. The acidulated alcohol is prepared by passing dry hydrochloric acid gas into cool 90 per cent alcohol until one cubic centimeter of the alcohol neutralizes about 2.3 cubic centimeters of normal alkali.

This method permits both potash and phosphoric acid to be estimated in a very small sample of material and has been tried over several years in the Bureau of Chemistry by many different analysts, both on soils and plants with the happiest results.

It has lately again been subjected to a critical examination by Veitch,⁹⁸ who applied it in comparison with the official method to 35 samples of soil with the following results:

TABLE I.—POTASH IN SOILS.

	Filtered on paper. acid alcohol.		Filtered on gooch crucible. Acid alcohol.	
	Official method. Per cent.	Moore method. Per cent.	Official method. Per cent.	Moore method. Per cent.
2134	0.39	0.42	2153	0.12
2135	0.27	0.27	2154	0.10
2136	0.18	0.18	2155	0.93
2137	0.52	0.65	2156	0.60
2138	0.41	0.40	2157	0.85
2139	0.23	0.24	2158	1.06
2140	0.14	0.12	2159	0.15
2141	0.27	0.34	2160	0.18
2142	0.29	0.27	2161	0.43
2143	0.29	0.27
Average	0.299	0.305	0.496
				0.497

⁹⁸ Journal of the American Chemical Society, 1905, 27 : 56.

	Plain alcohol.			Plain alcohol.	
2144	0.44	0.42	2162	0.48	0.48
2145	0.48	0.50	2165	0.08	0.09
2146	0.47	0.47	2166	0.38	0.41
2147	0.50	0.48	2168	0.44	0.48
2149	0.44	0.42	2169	0.21	0.21
2150	0.60	0.62	2170	0.21	0.22
2151	0.78	0.82	2171	0.11	0.12
2152	0.67	0.66	2172	0.10	0.11
Average	0.547	0.548	0.25	0.265
General average	0.41	0.41	0.38	0.39

The results are given just as they were obtained in the regular routine of the laboratory; they were not repeated nor were any rejected. In some cases the differences are larger than they should be between duplicates, but as the average results are practically identical it seems fair to consider such differences as due to the analytical work rather than to the method itself.

The results are not noticeably different where the filtration and washing were done on paper rather than on the gooch, and under some conditions the use of paper presents certain advantages as the potassium chlorplatinate may be dissolved in order to separate it from foreign salts, and the solution evaporated, dried and weighed in platinum dishes. The combined iron and aluminum oxids ranged from five to 25 per cent in these samples. No particular advantage appears to result from the use of the acidified alcohol as recommended by Moore, at least where the amount of lime salts, more especially calcium sulfate, is not large. It would appear, therefore, that the method may be further simplified by substituting ordinary 90 per cent alcohol for the acidified alcohol.

This method has many advantages over any other in use where only potash and phosphoric acid are to be determined.

401. Estimation of Total Alkalies and Alkaline Earths.—To properly determine the exact amount of these substances in a sample of soil it is necessary first to remove the silica. This is accomplished in the process of Berthelot and André⁹⁴ by intimately incorporating with the sample, in a state of very fine powder, four or five times its weight of ammonium fluorid, in a platinum

⁹⁴ *Annales de Chimie et de Physique*, 1888, [6], 15 : 89.

dish, and heating gently without passing a pasty state. After cooling the mixture, it is moistened with strong sulfuric acid and gently heated until all acid fumes have disappeared, but the mass is not raised to a red heat. If there is any doubt about the complete decomposition of the silica the treatment is repeated.

The results of treating soils with other solvents to ascertain the quantities of potash and other substances dissolved are also given in the article cited. The solvents used are water, sweetened water, acetic ether, acetamid, ammonia, carbonic acid, acetic acid, dilute hydrochloric acid, dilute nitric acid, dilute hydrochloric acid in motion, cold and hot, concentrated hydrochloric acid in motion, cold and hot, and pure nitric acid, cold and hot.

Comparison of Fluorin Method with Common Methods.—To establish the difference in the data obtained by the old and new processes samples of the same earth were treated by Berthelot and André by different methods with the following results:

	By the fluorin method. Per cent.	By the cold dilute hydrochloric acid method. Per cent.	By the concentrated hydrochloric acid method. Per cent.	By incineration and subsequent treatment with boiling hydrochloric acid method. Per cent.
Potash.....	0.886	0.021	0.149	0.176
Soda	0.211	0.024	0.033	0.042
Magnesia.....	0.087	0.033	0.033	0.067
Lime	1.160	0.879	1.120	1.060
Alumina.....	3.950	0.102	1.009	2.631
Ferric oxid	2.150	0.296	1.401	1.678

The impossibility of getting all the alkalies and oxids into solution by even the prolonged action of a boiling acid is clearly set forth in the above table. Boiling sulfuric acid might do a little better but would not give correct results. Lime alone of the elements in the soil can be correctly determined by solution in boiling hydrochloric acid, a circumstance due to the fact that lime is found chiefly as carbonate, sulfate, and phosphate in the soil, and these compounds are easily soluble in hot hydrochloric acid with the exception of the sulfate. Even lime could not be thus determined in soils containing silicates rich in lime. The other mineral elements cannot be entirely dissolved by the common methods. This is due to the forms in which they occur, being

mostly silicates of different composition, usually with excess of silica.

As to the silicates they may be divided into two groups. The first of these are the hydrated silicates, resembling the zeolites, capable of being completely decomposed by boiling acids. The first group of silicates is doubtless of greater importance to vegetable life than the second since it would, doubtless, give up its alkalies with greater ease. This distinction is, however, arbitrary. It is, in fact, impossible to place on one side the soluble and on the other, the insoluble silicates. This distinction represents only the unequal degrees in the speed of decomposition of the different silicates contained in the primitive rocks under the influence of atmospheric agents, the soil being nothing more than the products of the decomposition of these rocks with vegetable mold. The second group is insoluble in acids.

That part of the silicates least decomposed at any given moment will be attacked more easily by acids, while that portion whose decomposition has been pushed furthest will be more slowly attacked. The action of the acid will grow more feeble as the time of contact is prolonged, and after a time a point is apparently reached where the results are nearly constant. But it is evident that this distinction is purely conventional and bears no necessary or even probable connection with the quantity of alkali really assimilable by plants.

Vegetables, moreover, exert on a soil, for the extraction of its alkalies and other matters, chemical reactions peculiar to themselves, altogether distinct from the tardy action of atmospheric agents and still more distinct from the rapid action of mineral acids.

It is well known with what energy, it ought to be said with what admirable instinct, plants take from the soil the least traces of phosphorus, of sulfur, of potash, of iron, and other substances necessary to their sustenance.

These specific actions of vegetables on the soil merit, in the highest degree, the attention of analysts and agronomists. Their intervention plays a most important part in the restitution to the soil, by means of complementary fertilizers, the mineral elements removed by vegetable growth.

402. Estimation of Lime by the French Method.—The quantity of lime contained in the soil varies within wide limits. Sometimes this base is entirely absent to such a degree that it is even impossible to discover feeble traces of it. Sometimes it composes almost the whole of the earthy mass. Lime is found in the soil, principally in the state of carbonate. It is also found combined with organic matter under the form of humates, with sulfuric acid, silicic acid, etc. It is customary to estimate the lime as a whole, without distinguishing between the different states in which it exists. The quantity of material which is used in the method⁹⁶ prescribed by the sub-committee on methods of analysis of the consulting committee of the agricultural stations and laboratories of France varies in proportion to the amount of calcareous matter contained in it. For a soil which contains a large amount of lime, one or two grams is sufficient for the analysis. For a soil which is poor in calcareous matter ten or even 20 grams are necessary. The quantity of lime dissolved in a given soil differs according to the kind and strength of the acids employed and length of contact of the acid with the soil. The calcium carbonate, the sulfate, the nitrate, and the humate rapidly pass into solution when treated with acids as above, but this is not the case with calcium silicates which are attacked much more slowly. Sometimes the silicates give only an insignificant increase in the amount of lime, and in this case it is immaterial what process of solution is employed. For simplicity it is best to adopt the method of solution in boiling concentrated nitric acid, prolonging the boiling for a period of five hours. This method of operation is sufficient to bring into solution at one treatment, not only the lime, but also the potash and magnesia. After having heated with acid for the necessary time there are added in the capsule in which the solution takes place ten cubic centimeters of nitric acid and 50 cubic centimeters of water. The mixture is heated, collected upon a filter and the residue washed. To the filtrate, the volume of which should be from 400 to 500 cubic centimeters, a sufficient quantity of ammonia is added to render it slightly alkaline. There is formed a precipitate of alumina and of iron oxid containing phosphoric acid and also sometimes a trace of the lime combined with the same acid.

⁹⁶ *Annales de la Science Agronomique*, 1892, 8th year, 1 : 270 et seq.

In order to keep the whole of the lime in solution it is necessary to add a little acetic acid, about ten cubic centimeters more than is necessary to neutralize the ammonia which has been added. If the liquid is turbid on account of the presence of the iron and aluminum phosphates it is necessary to filter it. There is afterwards added a slight excess of ammonium oxalate in solution, and the whole is left for 24 hours in order that the calcium oxalate may deposit. The complete precipitation is not always immediate, and especially in the presence of magnesia it takes place with slowness. The calcium oxalate is collected upon a filter and washed with hot water. To determine the quantity of the lime the best procedure consists in transforming the oxalate into carbonate by a careful ignition, and afterwards heating to a high temperature for some time. The oxalate for this purpose should be contained in a covered platinum crucible. By this method the calcium carbonate is transformed into calcium oxid, in which form it is weighed rapidly to avoid absorption of moisture.

Instead of proceeding as above, the lime may be weighed as sulfate. For this purpose the calcium oxalate is transformed into carbonate by ignition in a platinum crucible. Afterwards it is treated with nitric acid until the carbon dioxid is completely driven off. The platinum crucible is covered with a funnel which is afterwards washed in order to bring back into the dish the small drops which have been projected in the process of boiling. An excess of sulfuric acid is added and evaporated to dryness on a sand-bath. Afterwards, in a muffle, the temperature is carried to a feeble redness until the vapors of sulfuric acid are all driven off. The lime is weighed in the form of sulfate, and the weight multiplied by 0.412 gives the lime contained in the quantity of soil used.

In special researches in which it is desired to avoid attacking the siliceous pebbles of the soil, the concentrated nitric acid is replaced by dilute nitric acid in slight excess, and heated for a few moments only. The calcium carbonate is then dissolved with the other calcareous salts not combined with silica in the rock products. The analysis is continued in other respects as just described.

403. Estimation of the Actual Calcium Carbonate.—The lime which is found in the state of carbonate plays one of the most important rôles in the chemical phenomena which take place in the soil. It is often of great importance to determine it. The most certain process is to estimate the carbon dioxid which is disengaged from the carbonate under the influence of an acid and to receive this gas in a jar graduated to measure it by volume. The flask recommended by the French Committee for this purpose contains about 300 cubic centimeters. The neck of the flask is connected with a condensing tube of about one centimeter interior diameter, which is cooled by a current of water.

According to the presumed richness in calcium carbonate varying quantities of soil are employed for analysis, from as little as half a gram for soils which are rich in carbonate, up to five or even ten grams for soils which are poor in carbonate. The apparatus is connected with a mercury pump for the purpose of exhausting the air as completely as possible therefrom. For this purpose the flask in which the carbonate is disengaged is made in the shape of a tubulated retort. Through the opening into the retort, a narrow tube is introduced and connected with a small funnel by means of a rubber tube supplied with a pinch-cock. When the retort has been connected with the mercury pump a slight vacuum is produced and the pinch-cock is opened and 40 cubic centimeters of distilled water allowed to enter. The pinch-cock is closed soon enough to retain a portion of the water in the funnel. The retort is then heated and a vacuum partially produced by means of the pump. When the flask is boiling, the steam drives out the air. A refrigerating jacket is connected with the tube leading from the retort to the pump by means of which the steam is condensed and falls back into the flask. After some minutes of boiling, a vacuum is produced; the lamp is then taken away and a cylinder, graduated at 100 cubic centimeters and filled with mercury, is placed over the lower orifice of the pump, and there is introduced into the apparatus, by the funnel above described, some hydrochloric acid in small quantities, but sufficient only to saturate the whole of the carbonate in the sample of soil. Usually three or four cubic centimeters will be sufficient. The acid should be added in such quantities as to pre-

vent the production of any large amount of foam. If frothing should be excessive a little oil can be added to the flask. The whole of the carbon dioxide produced in the reaction is withdrawn by means of the mercury pump and collected in the graduated jar. Towards the end of the operation the flask is heated anew in order to produce an ebullition which is continued for some time. The volume of gas collected is measured after making the proper corrections for pressure and temperature. Afterwards the carbon dioxide which has been produced is absorbed by two or three cubic centimeters of a solution of potash of 42° Baumé. This potash is introduced into the graduated jar by means of a pipette bent into the form of a U in the lower portion. If the whole of the gas is not absorbed the volume which remains is read, and this is subtracted from the original volume after having made the proper corrections for pressure and temperature. The difference gives the quantity of carbon dioxide contained in the amount of earth employed. From this the actual weight of the calcium carbonate is complete. This official French method does not appear to possess any advantage in accuracy to the usual absorption method and is far more complicated.

404. Estimation of the Active Calcareous Matter in Soils.—Like other soil elements, the calcium carbonate exists in different degrees of fineness and availability in the soil. It must be admitted that the fine particles play the most important rôle. The calcium carbonate, which exists in large fragments, presents only a circumscribed surface and remains almost inactive, although it is easily corroded by the rootlets of plants. It is possible to estimate in a rapid way, the quantity of fine carbonate in the soil, considering that in a time relatively short, feeble acids act upon calcareous matter proportionally to the surface which it presents, and that it attacks, therefore, especially the finest particles. By measuring the amount of carbon dioxide set free under the action of dilute acids it is possible to estimate the content of available calcareous matter in the soil.

The apparatus of Mondesir is recommended for this purpose by the French Committee. It is composed of a tubulated flask of about 600 cubic centimeters capacity. The interior tubulature carries a manometer fixed by means of a stopper. This is formed

of a rubber tube, terminated by a glass tube, whose extremity is united to a little rubber bag, very flexible, placed in the interior of the flask.

Graduation of the Apparatus.—If the apparatus is new it is necessary to begin by graduating it. The rubber bag is filled with water, the air being carefully excluded, in such a way that the level of the water comes just a little above the bend in the tube. There are placed in the flask 125 cubic centimeters of water and it is shaken for a few seconds. The flask and the manometer are then unstoppered and the level of the water in the manometer is made to equal the level of the water in the flask. With a rubber ring the level of the water in the manometer tube is marked. The manometer is then stoppered. There is added to the flask two-tenths gram of pure calcium carbonate. The flask is closed and shaken for a minute. There is then added, enclosed in a little piece of filter paper, six-tenths of a gram of pulverized tartaric acid and the flask immediately closed and shaken several times. The manometer tube is then uncorked and moved until the level of the water reaches the point marked before. The difference in level after the height of the water remains constant is then read. The depression in the level observed, corresponds to carbon dioxid from two-tenths gram of pure calcium carbonate.

405. Estimation of the Available Calcareous Matter in the Soil. There is introduced into the flask of the apparatus a quantity of soil varying in amount in accordance with the content of carbonate which it is supposed to contain. There are added 125 cubic centimeters of water and the flask is shaken for a minute. As in the test given before, the level of the water in the manometer is then made to correspond to that of the water in the flask. The level in the manometer is marked as before with a rubber band, and the manometer is closed. There are then added, contained in a piece of filter paper, two grams of pulverized tartaric acid and the operation is finished as described before. The amount of tartaric acid added, in general, should be three times as much as the amount of calcium carbonate supposed to be contained in the earth. The pressure in the manometer being proportional to the quantity of carbon dioxid disengaged, it is easy to calculate the

quantity of calcium carbonate in a state of fine division contained in the soil taken for the test.

In order to fill the rubber bag it is necessary to put it in its proper place in the apparatus. The flask is filled with water in order to flatten the rubber bag and expel the air from it. It is then closed with a cork. Afterwards, with the aid of a small funnel and with a copper wire placed in the tube, the lower extremity of which descends just to the elbow, the air in the tube is replaced by water. The operation is finished by uncorking the flask and inclining it or shaking it after a partial vacuum has been established. It is useless to attempt to drive off the last particles of the air. The rubber bag should have a content of about double the volume of the whole of the interior of the manometric tube. In the washing which is necessary between two successive operations, it is well to fill the flask entirely with water in order to expel all the carbon dioxid which it may contain.

The same remark may be made of this method of determination as was made of the last one. In the present case, however, the operation is not quite so complicated. When the apparatus is once arranged, it will admit of rapid determinations.

406. Lime Method at the Swedish Station.—A method of estimating lime in soils which is somewhat different in principle from those usually followed is employed in Sweden.⁹⁶

The lime solution is prepared by digesting 150 grams of fine soil with 500 cubic centimeters of a ten per cent hydrochloric acid solution for 48 hours with frequent shaking. The free carbonates which may be present are first neutralized with acid before beginning the operation above noted. The solution is poured on a dry filter and the lime determined in the filtrate in the following manner: Fifty cubic centimeters corresponding to 15 grams of soil are boiled in a 100 cubic centimeter flask with a little potassium chlorate, nearly neutralized with ammonia and boiled with sodium acetate with the purpose of precipitating the greater part of the iron silica and phosphoric acid. The mass is cooled rapidly, the volume made up with water to 100 cubic centimeters, poured on a dry filter and 50 cubic centimeters of the filtrate correspond-

⁹⁶ Experiment Station Record, 1894-95, 6 : 22.

ing to 7.5 grams of soil treated with an excess of acetic acid, and the lime precipitated hot by ammonium oxalate.

The precipitate is washed, dried and ignited for ten minutes over the blast-lamp, dissolved in an excess of standard hydrochloric acid solution, the excess of acid determined by titration, and the quantity of calcium oxid dissolved by the acid computed.

The principle on which this method is based is seen to be the precipitation and consequent separation of the lime in an acetic acid solution as oxalate, the conversion of the oxalate into oxid, and the determinations of the oxid from the quantity of acid required to convert it into chlorid.

407. Estimation of Assimilable Lime.—In the determination of the total lime in soils or even of that part present as carbonate, it is not to be assumed that the quantity assimilable by plants is known; particles of lime minerals in soils are corroded only superficially by the rootlets of plants and any process which would attack only the superficies of the lime particles would thus more nearly resemble the activity of the solvent forces of plant growth. Oxalic acid is a reagent of this kind, attacking only the surfaces of lime particles. Reverdin and de la Harpe guided by this fact have based a method for determining the amount of lime present in the soil in an available state on the solvent action of oxalic acid.⁹⁷ After the total lime content has been determined, 20 grams of the soil sample are covered with 200 cubic centimeters of a solution containing in molecular proportion a known quantity of sodium oxalate and carbonate. The mixture is digested on the water-bath for one hour. By this treatment all lime minerals are converted superficially into oxalate while particles containing magnesia are not affected. After filtering and washing well, the filtrate and wash-waters are acidulated with hydrochloric acid. If any precipitate of organic matter be produced it is separated by filtration. The filtrate is treated with a slight excess of sodium acetate by which process the excess of hydrochloric acid is replaced with acetic acid after which the oxalic acid may be separated by treatment with calcium chlorid and subsequently titrated with potassium permanganate in presence of excess of sulfuric acid. The oxalic acid obtained, deducted from

⁹⁷ Chemiker Zeitung, 1889, 13 : 726.

the quantity originally present will give the amount consumed on the surfaces of the lime particles and consequently the amount of lime corresponding thereto which may be considered as available for plant growth.

408. Method of the Halle Station for Lime.⁹⁸—a. *In Phosphates, Limestones, Etc.*—Four grams of the prepared sample are heated with 50 cubic centimeters of hydrochloric acid and five cubic centimeters of nitric acid, in a porcelain dish on the water-bath to dryness, and left for a few hours at 105° for the purpose of separating the silicic acid. The dry residue is moistened with hot water and a few drops of hydrochloric acid, and allowed to stand for some time with frequent stirring. The contents of the dish are then washed into a half-liter flask, which is filled up to the mark and the separated silica removed by filtration. If the silicic acid is not taken into account, the solution can be made directly in a half-liter flask.

After filtration, an aliquot part of the filtrate is neutralized in a 250 or 500 cubic centimeter flask with ammonia, again acidified with a few drops of hydrochloric acid and allowed to stand six hours at least, in the cold, with ammonium acetate. For each four grams of the substance 50 cubic centimeters of an ammonium acetate solution are used, made by dissolving in one liter of water 100 grams of ammonium acetate. If phosphoric acid is present in excess, iron and aluminum oxids are precipitated completely as phosphates. If iron and aluminum oxids are in excess, the excess must be precipitated by ammonia. If it is feared that in the subsequent precipitation of the lime by ammonium oxalate there may be still some phosphoric acid in solution, before precipitation with ammonium acetate the proper amount of ferric chlorid is added and the iron is afterwards precipitated with ammonia. It is certain that in the presence of oxalic acid and phosphoric acid the lime is precipitated as oxalate, but should it be feared that traces of calcium phosphate are precipitated with the iron and aluminum phosphates the precipitate of iron and aluminum phosphates may be dissolved in hydrochloric acid, neutral-

⁹⁸ Bieler and Schneidewind, Die agrikultur-chemische Versuchsstation, Halle a/S, Berlin, 1892 : 80.

ized with ammonia, again acidified and a second time precipitated with ammonium acetate and the filtrate added to that first obtained.

For the further estimation the filtrates are united and a quantity corresponding to a given part of the original sample, and being in volume from 50 to 100 cubic centimeters is made slightly acid with acetic acid and while hot precipitated with dilute ammonium oxalate. The filtrate must contain acetic acid since calcium oxalate is best precipitated from a slightly acetic acid solution. The filtering of the calcium oxalate should not take place until from six to 12 hours after precipitation, and during this time it should stand in a warm place. Filter paper of the best quality should be used for the purpose.

The dried precipitate is brought into a platinum crucible together with the filter; the filter is first incinerated over an ordinary Bunsen and the calcium oxalate converted into calcium oxid by ignition for 15 minutes over the blast. It is then cooled in a well-closed desiccator and weighed as oxid. If in the precipitation of the iron and aluminum phosphates sodium acetate be employed instead of ammonium acetate, the precipitation must take place hot and filtration also be accomplished on a hot filter.

b. *Estimation of Lime in Soils.*—For the estimation of lime in soils there may be used either the acid soil-extract, prepared as under the direction for the estimation of potash, or 20 grams of the soil may be treated with hydrochloric acid and a few drops of nitric acid, and evaporated to dryness in a porcelain dish and the silicic acid separated as described for the estimation of lime in phosphates and limestones. In the case of soils, iron and aluminum oxids can be precipitated directly with ammonia since the small quantity of phosphoric acid usually contained in soils is not sufficient to influence in any way the estimation of the lime. For example, suppose there is 0.10 per cent of phosphoric acid contained in a soil. In case the whole of this phosphoric acid is taken down with the lime it would only amount to about 0.10 per cent of calcium oxid precipitated as phosphate. This case, however, is very improbable since it is much more likely that the iron and aluminum phosphates will be precipitated and the whole of

the phosphoric acid be carried down with them instead of being precipitated with the lime.

The precipitation of the lime and its subsequent treatment are to be conducted as just described.

409. Estimation of Magnesia.—Magnesia usually is found in much smaller quantities than lime in the soil. It is necessary to operate upon considerable quantities of the sample in order to determine the magnesia with precision and especially when it occurs in minute proportions. The procedure recommended by the French Committee is as follows:⁹⁹ From ten to 20 grams of the soil are used. The decomposition is accomplished as in the case of the lime determination. A few drops of barium nitrate are added for the purpose of precipitating any sulfuric acid present. Some ammonia and ammonium carbonate are added to precipitate the iron and aluminum oxides, the lime and the excess of barium introduced, as well as the phosphoric acid. The operation is best conducted on a dilute solution having a volume of from 400 to 500 cubic centimeters. The solution from which the lime has been precipitated, contains with the magnesia, large quantities of ammoniacal salts which it is necessary to destroy. For this purpose the solution is concentrated in a flask until its volume is about ten cubic centimeters. About ten cubic centimeters of nitric acid are added and the whole brought to the boiling point, and a few drops of hydrochloric acid added. Continuing the heating, hydrochloric acid is added in small portions and, from time to time, some nitric acid until the bubbles indicating the setting free of gaseous nitrogen, resulting from the action of the nascent chlorine upon the ammonia, have completely ceased to appear. The whole is then evaporated on a sand-bath in a porcelain dish in order to separate the silica. The residue is taken up by water containing a few drops of nitric acid. The filtrate is evaporated to dryness in a covered porcelain dish. Upon the residue four or five grams of oxalic acid, in a state of powder, are placed and a little water is added in such a way that the moist mass covers the matter in the dish. In order to avoid all losses there is placed upon the dish a funnel which serves as a cover. The dish is heat-

⁹⁹ *Annales de la Science agronomique*, 1891, 8th Year, 1 : 275.

ed on a sand-bath, and when the film which is formed begins to break there are added from time to time, a little more oxalic acid and water until there is no longer any disengagement of the vapor of nitric acid. Afterwards evaporation is carried to dryness and the heat raised to a low redness. The magnesia is found in a free state or mixed with alkalies. It is washed with a small quantity of water and collected upon a very small filter paper. The filter paper is dried, burned, the ignition carried to redness and afterwards cooled and weighed. In order to test the purity of the magnesia it is transformed into sulfate by the addition of a few drops of sulfuric acid. The excess of sulfuric acid is driven off by heating moderately by means of a gas-burner moving it in a circular manner round the bottom of the capsule and lifting the cover from time to time in order to allow the vapors of sulfuric acid to escape. The weight of the magnesium sulfate should correspond to that of the magnesia from which it was formed. The substitution of a gooch in place of the filter paper will render the above process more simple.

Magnesia exists most often in the soil in the state of carbonate or silicate. In this last state it is especially abundant in some soils, such as those which are derived from mica schists, serpentines, etc. In treating earth of this last quality with concentrated, nitric acid, there is dissolved also a notable part of the magnesia of the silicates. If, however, it is treated for some minutes only with dilute hydrochloric acid the amount of magnesia present as carbonate alone can be estimated separately.

470. Method of the Halle Station.¹—For the estimation of magnesia the sample of soil or fertilizer is brought into solution in the same way as is given for the estimation of lime. After the separation of the silicic acid, the iron and alumina are precipitated in the presence of sodium acetate. In the case of phosphatic fertilizers, ferric chlorid should first be added in order that the excess of phosphoric acid shall be in all cases certainly combined with the iron. After this the lime is separated as usual with ammonium oxlate. After the precipitation of the lime, the magnesia is precipitated in an ammoniacal solution with sodium phosphate and the ammonium magnesium phosphate estimated exactly as in

¹ Bieler and Schneidewind, *Die agrikultur-chemische Versuchsstation, Halle a/S, Berlin, 1892* : 85.

the case with the estimation of phosphoric acid, as magnesium pyro-phosphate.

A simpler method for the estimation of magnesia consists in precipitating it as ammonium magnesium phosphate in the presence of a solution of ammonium citrate, the other bases remaining in solution. In this case the operation is carried on in an inverse way as described under the estimation of phosphoric acid, the proper quantity of the acid solution being neutralized with ammonia and after the addition of sodium phosphate, the required quantity of citrate solution added and a further excess of ammonia supplied.

411. Estimation of Manganese.—The estimation of manganese in the presence of Fe_2O_3 , Al_2O_3 , CaO , etc., presents peculiar difficulties. In ordinary alluvial clays the quantity of manganese is proportionately small and its estimation may be neglected. In volcanic clays the quantity of manganese, in proportion to the lime and magnesia, is much larger. One of the methods used in France for estimating manganese is that of Carnot.² The hydrochloric acid extract of the soil is evaporated to dryness and heated with potassium bisulfate in order to destroy the organic substance, the neutralized solution of the residue precipitated with 20 cubic centimeters of hydrogen peroxid solution and 30 cubic centimeters of ammonia. The colorless filtrate gives, with nitric acid and bismuth peroxid, no trace of reaction for manganese. The precipitate, which includes the manganese as 5MnO_2 , MnO is washed by decantation, treated with oxalic acid and dilute sulfuric acid, and the excess of oxalic acid titrated with potassium permanganate in the usual way. Each five equivalents of available oxygen found corresponds to six equivalents of manganese.

412. Estimation of Manganese by the French Method.—Manganese exists in all plants and its presence in small quantities seems necessary to vegetation. The method of estimation adopted by the French Committee is the one proposed by Leclerc and is applicable even when the base exists in small quantities.

In 20 grams of the soil the organic matter is destroyed by incin-

² *Comptes rendus*, 1888, 107 : 997 and 1150.

eration. In a flask of 200 cubic centimeters capacity, are placed the sample and 30 cubic centimeters of water and, little by little, some hydrochloric acid for the purpose of decomposing the calcium carbonate. When effervescence has ceased ten cubic centimeters of the same acid are added and boiled for half an hour, filtered, washed, and the wash-water and filtrate evaporated to dryness in a porcelain dish. There are added 20 cubic centimeters of nitric acid of one and two-tenths density, and ten cubic centimeters of water. The liquor is boiled with constant shaking. Afterwards there are thrown in, in two or three portions, ten grams of lead dioxid. The boiling is stopped just at the moment when all the lead oxid is introduced into the liquor and the mixture is then shaken vigorously. The manganese is transformed by this treatment into a highly oxygenized compound having a deep rose coloration. It is transferred immediately afterwards to a graduated cylinder of 100 cubic centimeters capacity, with the wash-waters the volume is completed to 100 cubic centimeters and it is vigorously stirred in order to obtain a complete homogeneity of the liquid. The stirring rod is withdrawn and the liquid left to settle. At the end of some minutes the principal part of the liquid is clear, and it is decanted by means of a pipette graduated at 50 cubic centimeters, and this quantity of the clear liquid is poured into a small glass precipitating jar to which is added immediately, with constant stirring, a solution of mercurous nitrate from a graduated burette. The addition of the nitrate is arrested at the moment when the rose color of the liquor disappears, and the volume of the mercurous nitrate employed is read from the burette.

It is now necessary to determine the strength of the mercurous nitrate, that is the quantity necessary to decolorize one milligram of manganese. For this purpose dissolve by means of five cubic centimeters of hydrochloric acid 150 milligrams of manganese dioxid, which is prepared perfectly pure by means of precipitation. When the solution is complete evaporate to dryness, add one cubic centimeter of sulfuric acid and heat on a sand-bath until white fumes of sulfuric acid appear. Redissolve in water and make the volume up to 100 cubic centimeters. Each cubic centimeter of this solution should contain one milligram of manganese.

Treat five cubic centimeters of this solution, equivalent to five milligrams of manganese, in a capsule with 20 cubic centimeters of nitric acid and ten cubic centimeters of water, add ten grams of lead dioxid, carrying on the operation exactly as described above. Fifty cubic centimeters of the solution are decolorized by the solution of mercurous nitrate, and thus it is easy to calculate the quantity of manganese which corresponds to one cubic centimeter of the mercurous nitrate employed. By a simple proportion the quantity of manganese contained in the 20 grams of soil is calculated.

The mercurous nitrate is prepared by dissolving five grams of crystallized mercurous nitrate in one liter of water; it is allowed to repose for some time and is preserved in a well-stoppered flask.

413. Estimation of Iron.—Iron, in general, is quite abundant in the soil where it is met with, principally in the state of anhydrous sesquioxid or the hydrated sesquioxid of silicates. Some soils, however, only contain iron in small proportions and it can happen that the introduction of iron as a fertilizing element may be useful. Plants assimilate iron only in small quantities, but it appears to be indispensable to their development and to the proper functional activity of their assimilating faculties. The method of estimation which is recommended is based upon the decoloration of potassium permanganate by iron in the ferrous state. The following description, based on the method proposed by the French Committee, will illustrate the process to be followed.

Ten grams of the soil are ignited in a porcelain capsule until all organic matter is destroyed. The ignited mass is then introduced into a flask of 100 cubic centimeters capacity with 30 cubic centimeters of hydrochloric acid and 15 cubic centimeters of water. It is boiled for about half an hour. The iron oxid is dissolved and is found in solution in the form of ferric chlorid. After filtering and washing, the volume of the filtrate is reduced by evaporation to about 25 cubic centimeters. The liquor is afterwards placed in a flask of from 100 to 150 cubic centimeters capacity, which is closed by a stopper carrying a tube furnished with a valve destined to prevent the re-entrance of the air. Ten cubic centimeters of dilute sulfuric acid are added from a mixture

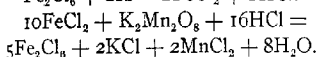
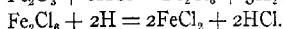
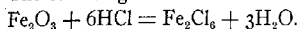
containing 20 cubic centimeters of strong acid and 80 cubic centimeters of water. Afterwards the iron is reduced to the ferrous state by introducing into the flask, in quantities of about five decigrams, metallic zinc and waiting after each addition until the portion last added is dissolved before adding another. This addition of zinc is continued until the iron is all reduced. When this point is reached and the last portion of zinc added is dissolved, the contents of the flask are transferred rapidly to a precipitating glass of about one liter capacity, in which there has been placed a little lately boiled but cold water. The flask is washed several times with cold water, previously boiled, to remove from it all traces of oxygen. The volume is made up to 500 cubic centimeters, and afterwards, without any loss of time, by means of a graduated burette and with constant stirring, a solution of potassium permanganate is added which is stopped exactly at the moment when the liquor begins taking on a light rose tint. The quantity of permanganate employed is read from the burette and is proportional to the amount of iron contained in the soil. A blank operation is made for the purpose of detecting traces of iron which the zinc may contain. If, as often happens, the soil contains a large amount of iron it is advisable to use only one gram of it for this operation. The aspect of the soil will indicate in general if it be very ferruginous, especially when the iron exists in the ferric state.

Preparation and Standardization of the Permanganate Liquor.—In one liter of water are dissolved ten grams of crystallized potassium permanganate and the quantity of iron which corresponds to one cubic centimeter of this liquor is determined. It may be well enough to remark that this liquor does not remain constant and it is necessary to titrate it from time to time. For this purpose pure piano wire may be used, being almost pure iron. One-tenth of a gram of this wire is dissolved in a flask in the manner recommended for treating the soil and with the same quantities of acid and water. When the solution is complete, it is transferred to the flask to be estimated, made up to one liter and permanganate added, just as in the case before mentioned, until the rose color persists. There is thus determined the quantity of iron which corresponds to each cubic centimeter of the permanga-

nate, and by a simple proportion, the quantity of iron contained in the soil analyzed is determined.

The Italian agricultural chemists proceed essentially in the same manner in determining the iron in soils, first igniting the sample and afterwards extracting the iron in the ferric state with boiling hydrochloric acid, reducing with hydrogen, and titrating with potassium permanganate.

The following are the reactions which take place:



Sulfuric may take the place of hydrochloric acid in the above reactions.

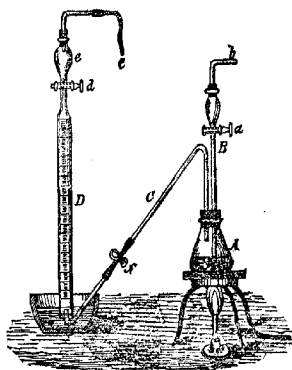


Fig. 82. Apparatus of Sachsse and Becker.

414. **Method of Sachsse and Becker.**²—Ferric oxid (not as silicate) in soils can be estimated by reducing with hydrogen, and measuring the hydrogen which is evolved by the action of the reduced iron on an acid. The sample of soil is weighed in a platinum boat, the boat put into a wide glass tube and heated in a stream of dry hydrogen. While this is going on, water is boiled in the flask *A* (see Fig. 82) from which the stopper has been re-

² Die landwirtschaftlichen Versuchs-Stationen, 1892, 41, 453.

moved, to drive out the air. When the reduction of the ferric oxid is complete, the boat is slipped out of the tube into the flask without interrupting the hydrogen evolution. In order to accomplish this without allowing the reduced iron to come in contact with the air the flask is inclined, the end of the glass tube inserted until it is covered with water and the boat is then dropped beneath the water. The flask is closed with a cork provided with a funnel tube, *B*, and a delivery tube, *C*; the cock *a* is opened, and tube *b* connected with a carbon dioxid apparatus from which the gas is passed into *A* until all the air is displaced. This point is determined by filling the burette *D* with potash-lye by aspiration at *C* and allowing the escaping gas from *C* to enter the burette as indicated in the figure. Any residual gas in *D* is removed by aspiration at *C* and allowing the potash-lye in *e* to enter in its place. The end of the tube *C* is placed under the measuring tube *D*, and the clamp *f* opened and the cock *a* closed. The funnel above *B* is filled with dilute, boiled sulfuric acid, the cork of *b* replaced and again connected with the carbon dioxid apparatus. The burner under *A* is lighted and acid let in. By continued boiling, all the hydrogen is driven into *D*, the carbon dioxid accompanying it being absorbed. The measuring tube is placed in a tall cylinder of water, the volume of gas read and reduced to 0° and 760 millimeters barometric pressure. To be certain that all carbon dioxid is absorbed, some fresh potash-lye may be introduced into *D* by carefully opening *d*. The iron is then computed from the volume and weight of the hydrogen by the formula (1) $\text{Fe} + \text{H}_2\text{SO}_4 = 2\text{H} + \text{FeSO}_4$.

If the substance analyzed contains iron silicates, these may be partly decomposed with formation of ferrous sulfate, according to the reaction (2) $2\text{Fe} + \text{Fe}_2(\text{SO}_4)_3 = 3\text{FeSO}_4$. This will redissolve a part of the metallic iron and yield ferrous oxid. In this case the contents of the flask are cooled in an atmosphere of carbon dioxid, made up to 500 cubic centimeters, of which 250 cubic centimeters are quickly filtered and titrated with permanganate. In order to properly distribute the iron in harmony with its previously existing states the following computations may be made:

Represent the ferrous oxid corresponding to formula (1) by x
 and that " " " (2) by z
 and that found by titration with permanganate (3) by a .

We have then the equation $x + z = a$. Since 72 parts by weight of ferrous oxid formed by formula (1) evolve two parts by weight of hydrogen, x parts of ferrous oxid would set free

$\frac{x}{36}$ parts of hydrogen; and this corresponds to the hydrogen found in the cylinder D ; viz., b .

If $a = \frac{1}{36}$ then $a x = b$ and by solving the equations we get $z = a - 36 b$ and $x = 36 b$. The ferrous oxid arising according to formula (2), however, is derived in such a way, that only one-third of it corresponds to metallic iron. Then: $x + \frac{1}{3} z = \frac{1}{3} a + 24 b$. For computing the total ferric oxid reduced by hydrogen there must, therefore, be added 24 parts by weight of hydrogen to one-third of the ferrous oxid found by titration with permanganate, and this quantity of ferrous calculated to ferric oxid. Some silicates, such as the micas, give ferrous oxid with hot dilute sulfuric acid. A correction for this is obtained by making one or more determinations without previously reducing with hydrogen.

The method of procedure above described appears to be capable of giving in an easily attainable manner some valuable indications of the state in which iron exists in a soil. While plants do not use any notable quantity of iron during their growth, nevertheless, its physiological importance is unquestioned. The chief points of difficulty to be considered are found in the changes which the iron may undergo even while heating in a stream of hydrogen, and the practical difficulties of obtaining carbon dioxid entirely free of air. The latter difficulty may be overcome by making blank experiments with carbon dioxid alone and estimating the volume of residual gas. The total volume of hydrogen obtained is then to be diminished by the ascertained amount.

In regard to the second point it is known that both ferrous and ferric oxids when ignited with hydrated silicates partly decompose and form new silicates. Care should therefore be taken not

to carry the temperature too high during the process of ignition.

415. Carnot's Method for Estimating Phosphoric Acid in Soils.—Carnot⁴ proposes the following procedure for the estimation of phosphoric acid in soils. The principle of this method depends upon the isolation of silica by the double precipitation of phosphomolybdate.

Ten grams of the sifted soil, dried at 100°, are charred if organic matter be present. The charred mass is moistened with water and afterwards with nitric acid, until the carbonates are decomposed. The mass is digested with ten cubic centimeters of nitric acid for two hours at about 100°, with frequent stirring and the addition of fresh acid, from time to time, to replace that which has been evaporated. After filtering and washing with hot water the filtrate is evaporated to a volume of 50 cubic centimeters and treated with five cubic centimeters of concentrated nitric acid and half a gram of crystals of chromic acid. After covering the dish with a funnel to return condensed vapors its contents are heated to the boiling point for half an hour to complete the destruction of organic matter. At the end of this time five grams of ammonium nitrate are added to facilitate the precipitation of the phosphoric acid, and 50 cubic centimeters of molybdate solution and the mixture kept at a temperature of about 100° for an hour. The precipitate obtained is washed twice by decantation with water containing one-fifth of its volume of ammonium molybdate solution. It is dissolved in 30 cubic centimeters of ammonia diluted with an equal bulk of warm water. The solution and the washings should measure 80 cubic centimeters and the ammonia therein is neutralized with nitric acid, keeping the temperature below 40°. When the yellow precipitate formed ceases to redissolve on stirring, that is when the ammonia has been neutralized, a mixture of three cubic centimeters of pure nitric acid and five cubic centimeters of water is added, together with the same quantity of molybdate solution. After standing for two hours at 40° the precipitate is brought upon a filter, washed first with water containing one per cent of nitric acid, and finally with a little pure water, and dried at 100° and weighed. A slight reduction of the phosphomolybdate, indicated by a blue tint

⁴ Buletin de la Société chimique de Paris, 1893, [3], 9 : 343.

when its edges come in contact with the filter paper may be neglected. The weight of the precipitate multiplied by the factor 0.0373 gives the quantity of phosphoric acid. The object of the second precipitation is to relieve the process of the necessity of rendering the silica insoluble, as the presence of silica in the solution as above treated does not interfere with the complete precipitation of the phosphate. This was proved by the author, by the introduction of considerable quantities of sodium silicate and these were found not to interfere with the accuracy of the operation.

The results are as accurate as those obtained by the methods of the consulting committee of the agricultural stations. The coefficient employed; *viz.*, 0.0373, is not the same as that recommended by the committee; *viz.*, 0.043. The committee, however, itself has recognized the inaccuracy of the latter number. The composition of the compound obtained by double precipitation according to Carnot is $P_2O_5 \cdot 24MoO_3 \cdot (NH_4)_2O + 3H_2O$.

416. Citrate Method of the Halle Experiment Station.—The available or easily soluble phosphoric acid in soils is estimated by Maercker and Gerlach, as follows:⁵

Sixty grams of the air-dried soil as prepared for analysis, are placed in an erlenmeyer with 300 cubic centimeters of two per cent citric acid solution and digested for 24 hours in the cold. It is necessary in this time to shake the flask four or five times and to put the stoppers in loosely in order to allow the escape of any evolved carbon dioxide. Of this mixture 200 cubic centimeters are filtered and evaporated in a 300 cubic centimeter dish to dryness. There remains, in most cases, a syrupy-like mass from which even by strong heating the silica is not completely separated. In order to reach this result the residue is treated with 20 cubic centimeters of concentrated sulfuric and five cubic centimeters of fuming nitric acid and heated over a bunsen. As soon as the appearance of foam denotes the beginning of the reaction the lamp must be removed. With strong foaming and the evolution of red-brown vapors the citric acid is completely oxidized. After the reaction is ended the contents of the dish are heated for

⁵ Die Agrikultur-Versuchs-Stationen, Halle, a/S, Berlin, 1892 : 70.

about 15 minutes over a small flame so that a continuous, yet not too violent evolution of sulfuric acid fumes takes place. After the silicic acid and the greater part of the lime have been rendered insoluble in this way the contents of the dish are diluted with water, stirred with a glass rod, washed into a 200 cubic centimeter flask, cooled, filled up to the mark, and filtered. From the filtrate, 100 cubic centimeters, corresponding to 20 grams of the sample are made slightly alkaline with ammonia, acidified by a few drops of hydrochloric acid, and after cooling treated with 50 cubic centimeters of the standard citrate of ammonia solution and 25 cubic centimeters of the standard magnesia mixture. The complete separation of the precipitate requires about 48 hours and shaking of the precipitate is not necessary. The incineration and weighing of the precipitate are conducted in the usual manner.

417. Estimation of Phosphoric Acid in Soils Soluble in Strong Acids.—The method of separating phosphoric acid directly in the presence of citrate of ammonia is regarded by the chemists of the Halle Station as incomparably more convenient than the older and more generally used process. At the Halle Station 25 grams of the soil sample are boiled with 20 cubic centimeters of nitric acid and 50 cubic centimeters of concentrated sulfuric acid for half an hour. With very clayey soils only half the quantity of the sample mentioned above is used in order to avoid the too great accumulation of soluble alumina. The oxidation of the organic substances of the soils must be carried on at a moderate heat to avoid foaming. During the boiling, the flask is to be often shaken to prevent the soil constituents from accumulating too firmly at the bottom. The total volume is finally made up to 500 cubic centimeters.

For the estimation, 100 cubic centimeters of the solution, corresponding to five (or two and a half) grams of the soil, are used. In order to nearly completely saturate the acid, the solution is treated with 20 cubic centimeters of 24 per cent ammonia, care being taken that the precipitate of iron and alumina which is formed is again completely dissolved. The solution is cooled and treated with 50 cubic centimeters of the citrate solution, and then

with 20 cubic centimeters of ammonia of above strength, and precipitated with the magnesia mixture. The filtration of the precipitate should not be made for at least 48 hours, during which time the flask should be often shaken to prevent the attachment of ammonium magnesium phosphate to its sides and bottom.

A detailed description of the citrate method for estimating phosphoric acid will be found in the chapter devoted to this subject under fertilizers in Volume Second.

418. French Method for Phosphoric Acid.—Phosphoric acid is found in the soil principally in combination with alumina and iron oxid, with organic matters, or with lime and magnesia. Whatever may be the state in which it is found all the phosphoric acid, with the exception of that which enters into the constitution of insoluble mineral particles, can be brought into solution by acids and determined by some of the approved methods. This method of solution, therefore, is capable of determining very accurately the total proportion of phosphoric acid in the soil, but it is incapable of rendering account to us of the state in which the phosphorus is found and of its aptitude to be utilized by plants.

The estimation of soil phosphorus, as recommended by the French Committee, is carried on in the following way.⁶ Twenty grams of the earth are submitted to ignition in a muffle heated to the temperature of redness but not higher. This calcination eliminates the organic materials, whose intervention in subsequent reactions might be able to prevent the precipitation of a part of the phosphoric acid. The calcined earth is placed in a dish of about 11 centimeters diameter and saturated with water. There is then added in small quantities, as long as effervescence is produced, nitric acid of 36° Baumé. When the effervescence has ceased, after thorough shaking and the addition of a new quantity of acid, it will be found that the whole of the calcium carbonate in the soil has been decomposed. It is necessary then to proceed to the solution of the phosphoric acid by adding 20 cubic centimeters of nitric acid and heating on the steam-bath for five hours, shaking from time to time, and avoiding complete desiccation. At the end of this time the whole of the phosphoric acid has entered into

⁶ *Annales de la Science Agronomique*, 1891, 1 : 267.

solution. It is taken up by warm water, filtered, and the insoluble residue washed with small quantities of boiling water. But from the solution obtained, which holds in addition to phosphoric acid, some oxid of iron, alumina, lime, magnesia, etc., it is necessary to separate the silica which has passed into solution. For this purpose the mass is evaporated to dryness on a sand-bath, heating toward the end of the operation with precaution and not allowing the temperature to pass beyond 110° - 120° . In these conditions there is obtained a magma which sometimes remains quite syrupy when the earth is very highly impregnated with calcium carbonate, but in which the silica is insoluble. It is indispensable that it be eliminated wholly because it would introduce grave errors into the results, as will be seen later on. If the temperature be carried too high during the desiccation this silica would react upon the earthy salts and alkaline earths forming silicates and it would be found ultimately again in solution. The application of a too high temperature would also render somewhat insoluble in nitric acid the iron and aluminum oxids, and these would retain small quantities of phosphoric acid. The desiccation, therefore, requires to be conducted with great precaution. When it is accomplished there are placed in the dish five cubic centimeters of nitric acid and five cubic centimeters of water, and the whole heated on the sand-bath until the entire amount of iron oxid is dissolved. The solution is filtered and washed with small quantities of boiling water in such a way that the total volume of the filtrate will not exceed from 25 to 35 cubic centimeters. Afterwards there are added 20 cubic centimeters of ammonium nitromolybdate and the whole is left at rest for 12 hours at the ordinary temperature. At the end of this time the phosphoric acid is precipitated in the form of ammonium phosphomolybdate. In order to be certain that an excess of nitromolybdate has been used in the precipitation, which is indispensable to the total precipitation of the phosphoric acid, a few cubic centimeters of the filtrate are removed by means of a pipette and are mixed with their own volume of the ammonium nitromolybdate. If, at the end of an hour or two, no precipitate is formed the operation can be regarded as terminated.

In order to collect and weigh the ammonium phosphomolyb-

date some precautions are necessary. Two smooth filters are used, one of which serves as a counter-weight for the other on the balance. After bringing the free contents of the dish onto the filter the part of the phosphomolybdate adhering to the dish is detached by the aid of a stirring rod, one of the ends of which is covered with a piece of rubber tubing. The washing is accomplished with very small quantities of water containing five per cent of its volume of nitric acid. When all of the precipitate is collected upon the filter and the washing is terminated a few drops of water are thrown upon the upper borders of the filters to displace the acid liquor which has been used in washing. The filters are then carried to the oven where they are dried at a temperature not exceeding 90° . The application of a higher temperature would decompose the ammonium phosphomolybdate and lead to results which would be too low. After the drying is completed the two filters are separated and placed upon the pans of the balance and the weight of the ammonium phosphomolybdate ascertained. This, multiplied by the coefficient 0.043, (0.0373 see page 453) gives the quantity of phosphoric acid contained in the weight of the soil which has been employed. The ammonium phosphomolybdate is pure if all the silica has been eliminated, but if a part of that has remained in solution it would furnish an ammonium silicomolybdate whose weight would be added to that of the phosphomolybdate. The elimination of the silica, therefore, should be made with the greatest care.

Different processes have been proposed in order to determine the forms under which phosphoric acid should be regarded as most assimilable. This problem is fully discussed elsewhere. The solubility of phosphoric acid in these different reagents gives information in regard to its state, but the relations which exist between this solubility and the assimilability of the acid can only be determined by comparisons with pot and field experiments.

Preparation of the Ammonium Nitromolybdate.—One hundred grams of molybdic acid are dissolved in 400 grams of ammonia of a density of 95. The mixture is filtered, and the filtered liquor is received drop by drop in 1,500 grams of nitric acid of one and two-tenths density, constantly stirring. This mixture is left standing for some days in an unexposed locality, during

which time a deposit is formed. The clear part is decanted and used.

The above method of the French chemists unfortunately attempts to determine the phosphorus content of the soil by weighing the yellow precipitate and using an empirical factor for the calculation, a factor which is probably too high.

Experience has shown that at this point it is far more accurate to continue the process by dissolving the yellow precipitate, and subsequently obtaining the phosphoric acid in combination with ammonia and magnesia, or according to the process of Pemberton the content of phosphoric acid in the yellow precipitate may be determined by titration. In regard to the latter method which will be given in full in Volume Second, it may be said that it has been found quite accurate by several analysts, although it is important that a precipitate which is so variable in its constitution should be secured under standard conditions in order to secure an exact determination by titration.

419. Petermann's Method for the Estimation of the Phosphoric Acid Soluble in Alkaline Ammonium Citrate.⁷—From 25 to 50 grams of the sample of soil are titrated with 100 cubic centimeters of alkaline ammonium citrate and placed in a flask of 250 cubic centimeters capacity, and allowed to digest for one hour at a temperature of from 35°-40°. The citrate solution is made as follows: Dissolve 500 grams of citric acid in concentrated ammonia of 0.92 density in sufficient quantity to secure a neutral reaction. The solution is reduced to a density of 1.09 at 15°, and there is added for each liter thereof 50 cubic centimeters of strong ammonia (0.92 specific gravity). After cooling the soil solution mentioned above, make up to the mark, filter, evaporate 200 cubic centimeters of the filtrate to dryness on a sand-bath in a platinum dish, burn lightly at first, and afterwards at a higher temperature. Take up the residue of the incineration with water and about two cubic centimeters of nitric acid, heat a few minutes gently, filter into a bohemian flask and precipitate with 50 cubic centimeters of ammonium molybdate solution in nitric acid, and estimate the phosphoric acid in the usual way.

⁷ L'Analyse du Sol, Brussels, 1891: 20.

420. Method of Dyer for Total and Assimilable Phosphoric Acid.⁸—For the determination of phosphoric acid, soluble in citric acid, secured as described in paragraph 367, 500 cubic centimeters of the filtrate obtained, corresponding to 50 grams of the soil, are evaporated to dryness in a platinum dish, gently ignited, dissolved with hydrochloric acid, again evaporated, redissolved and filtered, and the phosphoric acid determined below as in the method applied to the hydrochloric acid extract of the soil itself.

The total phosphoric acid soluble in strong acids is determined in each case in ten grams of the dried soil and also in 25 grams, the mean of the two results being taken. The numbers obtained in each case are, however, all but identical, the difference in the duplicate percentages being in most cases, only a small one in the third place of decimals.

The soil is incinerated and digested with hydrochloric acid, and evaporated to dryness, redigested with acid, filtered, and washed. The filtrate and washings are concentrated to a small bulk, and treated, in the cold, with excess of a solution of ammonium molybdate in nitric acid. After standing 48 hours, the liquor is decanted through a filter, the precipitate washed several times by decantation, first with one per cent nitric acid, then with pure water in very small doses, and finally transferred to the filter and washed free from excess of acid. The ammonium phosphomolybdate is dissolved in ammonia, evaporated to dryness in a platinum capsule, adding water once or twice, and dried to constant weight at 100°. The residue contains three and one-half per cent of its weight of phosphoric acid. This is the method of Lehner; and for determining small quantities of phosphoric acid, such as occur in soils or in solutions of iron and steel, is in the opinion of Dyer very much to be preferred to the old-fashioned method of conversion into magnesium ammonium phosphate. The solubility of the yellow precipitate in the small quantity of wash-water used is in most cases negligible. As a matter of fact, the quantity of wash-water used in these analyses was found capable of dissolving only 0.005 gram of precipitate, of which only 0.00017 is phosphoric acid, making an error of 0.0017 per cent on the soil if ten grams be used, or of only 0.0006 if 25 grams be used. In the citric acid

⁸ Journal of the Chemical Society, Transactions, 1894, 65 : 140.

experiments the solution from 50 grams of soil is used, when the error due to solubility of precipitate shrinks to 0.0003 per cent. The correction for this solubility is, however, made in each case.

It may be observed that the method of *Hehner* is not applicable if the molybdic solution be added to a hot liquid, since, in that case, some molybdic acid is sure to crystallize with the yellow precipitate. Moderate and careful warming to about 35° hastens precipitation, but it is preferable, when speed is not a special object, to precipitate cold, and leave the beaker standing at the laboratory temperature over night, or longer if the quantity to be determined is very minute. The objections to heating a soil before the extractions of its easily soluble constituents have already been pointed out and apply also to the above process.

421. Methods of Berthelot and André.⁹—The phosphorus in the soil may be found under four forms; *viz.*,

1. Phosphoric acid in phosphates.
2. Phosphoric acid in compound ethers similar to phosphoglycerates which dilute acids and alkalies decompose slowly with regeneration of phosphoric acid.
3. Mineral compounds of phosphorus of the order of phosphites and hypophosphites which are resolved by oxidizing solutions like nitric acid with formation of phosphoric acid but which are only oxidized to this state by the reagents employed after a contact of indefinite length and uncertainty.
4. In the form of organic compounds of the order of the oxid of triethylphosphine, phosphorated phenyl compounds and cerebrie acid. These compounds are transformed into phosphoric acid with extreme difficulty by the usual reagents employed in the wet way.

It is, therefore, seen that the promiscuous employment of oxidizing agents for the valuation of phosphoric acid in soils and vegetables is not a very reliable procedure. The same is true after incineration by which more or less phosphorus may be lost or rendered insoluble in acids. For analytical purposes the phosphorus is assumed to exist in the three special forms mentioned

⁹ *Annales de Chimie et de Physique*, 1888, [6], 15 : 128.

Berthelot, *Chimie végétale et agricole*, Paris, 1899, 4 : 83.

below. The methods used by Berthelot and André for the estimation of these forms of phosphorus are as follows:¹⁰

Total Phosphorus.—The sample is at first oxidized by a current of air near a red heat and the vapors are conducted over a column of sodium or potassium carbonate at the same temperature. The combustion is finished in a current of pure oxygen. All phosphorus compounds, even those which are volatile, are by this treatment converted into phosphoric acid. The part of the acid held by the carbonate is to be determined with the non-volatile portions.

A less certain method of oxidation consists in mixing the material with potassium nitrate and carefully throwing it little by little into a red hot platinum crucible.

Estimation of the Phosphoric Acid Pre-existing as Phosphates.—The sample is treated with a cold dilute acid incapable of exercising an oxidizing or decomposing effect on the ethers. The dissolved phosphoric acid is precipitated and weighed in the usual way. The precipitate first obtained should be ignited and the phosphoric acid taken up and reprecipitated. This is necessary to remove any organic matter or silica which the first precipitate may contain.

Estimation of Ethereal Phosphoric Acid.—The sample is boiled for some time with a non-oxidizing acid or with a concentrated solution of potash. The phosphoric acid dissolved represents that which was present as phosphates and as ethers. From this, deduct that portion pre-existing as phosphates, ascertained as above, and the remainder represents the part derived from the ethereal compounds.

Estimation of Phosphorus in Organic Compounds and Special Minerals.—From the total phosphoric acid deduct that found as phosphates and ethers. The difference represents the quantity combined as noted in the caption. Illustration.

A sample of soil contained:

	Per cent.
Total phosphoric acid	0.292
Of this, pre-existing as phosphoric acid.....	0.109
As ethereal phosphoric acid.....	0.074
As organic phosphoric acid	0.109
Sum.....	0.292

¹⁰ *Annales de Chimie et de Physique*, 1892, [6], 25 : 303.

422. Method Used at the Riga Station.—In the method pursued at the experimental station at Riga¹¹ the organic matter in the fine earth is first destroyed by igniting 25 grams in a muffle. The ignited residue is placed in a 250 cubic centimeter erlenmeyer and digested with 150 cubic centimeters of ten per cent hydrochloric acid for 48 hours with frequent shaking. The filtrate is evaporated to dryness in a porcelain dish to separate any dissolved silica, the residue taken up with dilute hot nitric acid, filtered, and the phosphoric acid precipitated with nitro-ammonium molybdate. The final weighing is made as magnesium pyrophosphate, following the usual procedure in respect of precipitation and washing. Experiments show that approximately 95 per cent of the phosphoric acid is obtained by one extraction and five per cent by a second, conducted exactly as the first. Thoms draws the following conclusions from a long series of determinations:

(1) For the simple purpose of determining the need of a soil for phosphatic fertilizer a single extraction with ten per cent hydrochloric acid is sufficient. The difference between the first and second extraction; *viz.*, from five to six per cent is too small to be of any value from a practical point of view.

(2) A soil which has been ignited until organic matter is destroyed gives up to the hydrochloric acid solvent about 14 per cent more phosphoric acid than a non-ignited sample would. This is in accord with the experience of the Bureau of Chemistry which shows that heating increases the solubility of some of the mineral ingredients of soil.

(3) The mean temperature in the flask during extraction on a steam-bath is 74°.

423. Method of Hilgard.¹²—A suitable quantity of soil (usually from three to five grams) is ignited in a platinum crucible, care being taken to avoid all loss. The loss of weight after full ignition gives the amount of chemically combined water and volatile and combustible matter.

The ignited soil is now removed to a porcelain or glass beaker, treated with four or five times its bulk of strong nitric acid, di-

¹¹ Thoms, *Zur Wertschätzung der Ackererden*, Second Contribution, Riga, 1893 : 114.

¹² Bulletin No. 38, Division of Chemistry : 80.

gested for two days, evaporated to dryness, first over the water-bath and then over the sand-bath, moistened with nitric acid, heated and treated with water. After standing a few hours on the water-bath it is filtered and the filtrate is evaporated to a very small bulk (ten cubic centimeters) and treated with about twice its bulk of the usual ammonium molybdate solution, thus precipitating the phosphoric acid. After standing at least 12 hours, first at a temperature of about 50° , the precipitate is collected on a filter and washed with a solution of ammonium nitrate acidified with nitric acid. The washed precipitate is dissolved on the filter with dilute ammonia water. After washing the filter carefully, the ammoniacal solution is treated with magnesia mixture, by which the phosphoric acid is precipitated. After allowing it to stand 24 hours the precipitate is brought onto a filter, washed in the usual way, dried, ignited, and weighed as magnesium pyrophosphate, from which the phosphoric acid is calculated. When a gelatinous residue remains on the filter after dissolving the phosphomolybdate with ammonia it may consist either of silica not rendered fully insoluble in the first evaporation, or, more rarely, of alumina containing phosphate. It should be treated with strong nitric acid, and the filtrate with ammonium molybdate; any precipitate formed is, of course, added to the main quantity before precipitating with magnesia solution.

424. Separation of Phosphoric Acid from Iron and Alumina.—

The following methods are among the first of the exact methods suggested for the complete separation of the phosphoric acid from the iron and alumina in soil analysis, where large quantities of these bases are found in solution:¹³

1. After the separation of the greater part of the iron and alumina the phosphoric acid is precipitated from the solution in nitric acid by molybdic acid. The process is carried on as follows:

The acid extract is heated in a flask to boiling and the remaining ferric oxid completely reduced by the gradual addition of small particles of sodium sulfite. While still warm the free acid is neutralized with soda-lye, and ammonia added until the fer-

¹³ Zeitschrift für analytische Chemie, 1864, 3 : 94.

rous hydroxid and the aluminum hydroxid are completely separated. Acetic acid is added in excess and until about four-fifths of the whole precipitate have passed again into solution. Then, after boiling for a moment, the whole is quickly filtered through a large filter with a cover, and the contents of the filter finally washed slightly. All the phosphoric acid is thus obtained in combination with some alumina and a very little iron. Nearly the whole of the iron and the larger part of the alumina, by this precipitation, are found in the filtrate and therefore cannot disturb the estimation of phosphoric acid in succeeding portions. The filter is filled with boiling water and a little nitric acid added and the dissolved precipitate is received in a beaker. The precipitation of the phosphoric acid is then accomplished by ammonium molybdate in the presence of nitric acid. After 24 hours all the phosphoric acid is thus precipitated and the precipitate is free from iron.

2. In the method of Schulze¹⁴ the iron is completely, and the alumina, with the exception of a small quantity, separated, and the precipitation of the phosphoric acid is accomplished either by the addition of a small quantity of tartaric acid and afterwards magnesium sulfate, or directly when it is desired to avoid the use of tartaric acid by means of ammonium molybdate. The principle of the separation of the iron and alumina depends on the fact that when the hydrochloric acid solution is nearly neutralized with soda or ammonia, and boiled after treatment with ammonium formate, the greater part of the alumina remains in solution, while the iron and phosphoric acid are precipitated. The precipitate is quickly filtered, washed with hot water, dried, taken from the filter and fused in a silver crucible with pure caustic alkali, either soda or potash. On solution and boiling with water, the iron is completely separated from the phosphoric acid, and from the small quantity of the alumina present and the precipitation of the phosphoric acid can now be accomplished, either by saturation of the alkaline solution with hydrochloric acid and the direct addition of the magnesia solution after the addition of a

¹⁴ *Zeitschrift für analytische Chemie*, 1864, 8 : 94.
Chemisches Centralblatt, 1861 : 3.

little tartaric acid and ammonia, or after the addition of nitric acid by ammonium molybdate.

In connection with this method of treatment attention is called to the fact that simple incineration of a compound containing organic phosphorus is not sufficient to secure all the phosphorus as phosphoric acid.

425. Matters Soluble in Sulfuric Acid.—It will have been noticed that of mineral acids, hydrochloric and nitric have been most frequently proposed as solvents for soil. Sulfuric acid has some advantages as a solvent, being in many respects more regular in its action and more sure in its results than those usually employed. When employed with a little mercury the organic matter contained in the sample is completely destroyed usually at the end of an hour. Moreover, the true clay (argile) is completely dissolved at the end of two hours, and any lime present is rapidly transformed into sulfate.¹⁵ Only the silica and certain of the silicates will resist the action of the acid. Hence, by a three hours digestion of the soil at a boiling temperature all of the fertilizing elements of the sample pass into solution, while those elements unimportant as plant foods remain undissolved. The heating of the sample is begun at a low temperature, when any sulfurous acid that may arise from the reducing action of the organic matter will be given off. The heat is gradually increased with frequent shaking of the flask to avoid caking until the sulfuric acid begins to boil, usually about an hour. The boiling should be continued for three hours. In the dissolved part of the sample are found the total nitrogen, phosphoric acid, potash, soda, lime, magnesia and iron. It is better, however, to treat a second portion of the sample with acetic acid to obtain the lime and magnesia. The estimation of the dissolved constituents of the soil is conducted by any of the standard methods. This process is much like that of Goss.

426. Method of Goss.—On account of the length of time required to determine the phosphoric acid in soils by the usual methods, Goss¹⁶ has proposed the following modification which in his hands has given satisfactory results:

¹⁵ Aubin and Alla, *Encyclopédie chimique*, 4 : 174.

¹⁶ Bulletin No. 43, Division of Chemistry : 58.

Place ten grams of the air-dried soil, which has been sifted through a one millimeter-mesh sieve in a pear-shaped, straight necked, kjeldahl digestion flask, which has been marked to hold 250 cubic centimeters. Add approximately seven-tenths gram of yellow mercuric oxid and from 20 to 30 cubic centimeters of concentrated sulfuric acid, as for the determination of nitrogen. Twenty cubic centimeters of acid are nearly always sufficient, but in the case of unusually finely divided clay soils containing little or no sand it is necessary to use 30 cubic centimeters to prevent caking of the contents of the flask. In doubtful cases 20 cubic centimeters of acid should first be added and at the end of five or ten minutes, if the contents show a tendency to cake, ten cubic centimeters more should be introduced. Thoroughly mix the contents of the flask by shaking, place on a suitable support over a burner, boil for one hour, cool, add about 100 cubic centimeters of water, five cubic centimeters of concentrated hydrochloric acid, and two cubic centimeters of concentrated nitric acid, boil gently for two minutes to oxidize iron, cool, make up to volume and filter through a dry folded paper until perfectly clear. In order to secure a clear filtrate it will usually be found necessary to pour the first portion of the filtrate back through the paper three or four times. Transfer 100 cubic centimeters of the filtrate to an ordinary flask of about 450 cubic centimeters capacity, add strong ammonia until a permanent precipitate forms, then six or eight cubic centimeters of nitric acid to dissolve the precipitate, and boil until clear. In the case of many soils it is not absolutely necessary to oxidize with hydrochloric and nitric acids, as a clear solution can be secured at this point without further oxidation. In the case of some soils, however, and especially in subsoils, the solution cannot be cleared up even by prolonged boiling with nitric acid, but if the solution have been previously oxidized, a clear solution can be secured without any difficulty whatever. Remove the flask from the lamp and after two minutes add 75 cubic centimeters of molybdate solution, place the unstoppered flask in an open water-bath kept at a temperature of 80° for 15 minutes, shaking vigorously four or five times while in the bath; then remove, let stand ten minutes to allow the precipitate to settle, filter through a nine centimeter filter avoiding too strong a pressure at

first, wash the flask and precipitate thoroughly with ammonium nitrate solution, place the flask in which the precipitation was made under the funnel, shut off the vacuum and close all the valves to the filtering jar to form an air-cushion and prevent too rapid filtration, fill the filter two-thirds full of hot water, add a few cubic centimeters of strong ammonia, and aid solution, if necessary, by stirring the precipitate with a small glass rod.

As pointed out by Hilgard, aluminum is sometimes carried down with the phosphoric acid upon precipitating with molybdate solution, in which case some of the phosphoric acid will not be dissolved in the treatment with ammonia. This will be indicated, first, by the appearance of a white precipitate upon dissolving the yellow precipitate in ammonia; and, second, by the difficulty experienced afterward in washing. If such a precipitate be present in any appreciable quantity, proceed as follows:

After washing out all the ammoniacal solution in the usual manner, place a small beaker under the funnel, close all valves, fill the filter one-third full of hot water, add the same amount of concentrated hydrochloric acid, and receive the solution and washings in the flask used for the former precipitation with molybdate solution, add 20 cc. of strong ammonium nitrate solution, neutralize with ammonia, clear up the solution with nitric acid, precipitate with 50 cc. of the molybdate solution, as before. Filter and wash the yellow precipitate as before, dissolve in ammonia, and add to the first portion. A third treatment may sometimes be necessary. As soon as the yellow precipitate is dissolved open the valve to the filtering jar but do not turn on the pump; after the solution has all passed through rinse the filter once with a small amount of hot water; after the last portion has passed through remove the flask and place a lipped beaker under the funnel and heat the solution in the flask to boiling. If the solutions have not been oxidized, a blue color is sometimes present upon dissolving the yellow precipitate in ammonia. This can be discharged by boiling the ammoniacal solution for a minute or two and shaking at the same time. Again pour the solution through the filter, avoiding use of the pump at first, otherwise loss from spattering is likely to ensue, wash out the flask and filter with a small amount of hot water, (the total filtrate should not

exceed 50 cubic centimeters), add hydrochloric acid to the contents of the beaker while hot, until the yellow color appears, then add a few drops of ammonia until the solution clears, cool, add an excess of filtered magnesia mixture from a burette, a drop at a time with constant stirring, let stand 15 minutes, add 20 cubic centimeters of strong ammonia specific gravity 0.90, let stand over night, filter, wash the precipitate with dilute ammonia, dry, ignite intensely over blast-lamp for ten minutes, cool in desiccator and weigh the $Mg_2P_2O_7$ secured.

Time of Digestion.—Experience has shown that very little phosphoric acid is extracted from the sample by digestion with sulfuric acid after the first 30 minutes.

Time Required to Precipitate Phosphomolybdate.—When the yellow precipitate is obtained according to the method of Goss practically the whole of it will be thrown down in five minutes.

Agreement with Standard Methods.—Comparative tests of the Goss method against standard methods have shown that it gives almost identical results with them. The variations were never more than from 0.02 to 0.03 per cent.

While this method has not been sufficiently tried to receive unconditional recommendation it possesses merits which entitle it to the attention of analysts. The method of preparing the reagents is the same as described in volume second of this work in the official method of determining phosphoric acid.

427. Volumetric Method of Estimating Phosphoric Acid in Soils.

—The principles which underlie the volumetric method of determining phosphoric acid will be discussed in full in volume second of this work. The method as applied to soils has been worked out by Williams.¹⁷ The soil extract is prepared by any of the methods already described, and in all cases especially when organic acids or salts are used in the extraction, the organic matter must be destroyed, either by oxidizing agents, or where great quantities are present as is the case when organic solvents are employed, by evaporation to dryness and ignition. After dissolving and filtering the residues after the organic matter is removed

¹⁷ Bulletin No. 119, North Carolina Agricultural Experiment Station : 279.

they are made up to known volume and portions equivalent to from one to 20 grams of the soil, according to the quantity of phosphoric acid present, removed for analysis.

In all cases the phosphoric acid is obtained by precipitation with a molybdate solution and washed free of any adhering acid. The precipitate (and adhering filter) is titrated directly with potassium hydroxid in excess and the remaining alkali determined by titrating with nitric acid using phenolphthalein as indicated. The details of the process are found under phosphoric acid in volume second. Excellent results comparable in accuracy with those obtained by the gravimetric method can be secured by this method in the hands of an experienced analyst, and it secures a great saving of time, especially when large numbers of analyses are to be done. It is considered especially applicable to those analysis where small quantities of phosphoric acid are involved.

428. Estimation of the Sulfuric Acid.—Sulfuric acid is generally present in small proportions in soils. Since the plants have need of sulfur it is proper to inquire into the presence of the compound which is its principal source. It is in combination with lime that sulfuric acid almost always exists. In addition to this there is also some sulfur combined with the organic matter of the soil.

By digesting a soil for six hours with hot, concentrated nitric acid the sulfates are dissolved, and there is transformed into sulfuric acid an important part of the sulfur which is combined with the humic substances. The quantity of soil to be operated upon should be about 50 grams.

After filtering and washing with hot water the filtered liquor is collected, in the French Committee method, in a flask and carried to boiling, and five cubic centimeters of a saturated solution of barium chlorid or sufficient to be in slight excess are added. The boiling is continued for some minutes and the flask is allowed to stand for 24 hours. The filtrate is received upon a filter and washed with boiling water, the filter dried and incinerated, allowed to cool, and as there may have been a slight reduction of the sulfate a few drops of nitric acid are added and a drop of sulfuric acid. It is now evaporated to dryness on a water-bath,

heated to redness for a few moments, cooled and weighed. The weight of the barium sulfate multiplied by 0.3433, gives the quantity of sulfuric acid obtained from the 50 grams of soil.

If it is desired to estimate only the sulfur which exists in the form of sulfate it is necessary to treat the soil with hydrochloric acid in a very dilute state, heating for a few moments only and afterwards precipitate by barium nitrate. If, on the other hand, it is desired to estimate the total sulfur which is sometimes of great interest, it is necessary to employ the process of Berthelot and André.

429. Method of Berthelot and André.—Sulfur may exist in the soil in three forms; *viz.*,

1. Mineral compounds, consisting generally of sulfates and in exceptional cases in marshy localities of sulfids of the metals and hydrogen sulfid.
2. Sulfur, existing in ethereal compounds or their analogues, as in urine, and mustard.
3. Organic compounds containing sulfur.

Estimation of Total Sulfur.—The principle on which this operation, as described by Berthelot and André, rests is that already described for phosphorus; *viz.*, oxidation in a current of oxygen and passing the vapors over a column of alkaline carbonate at or near a red heat.¹⁸

The ordinary methods of oxidation in the wet way give generally inexact results.

Estimation of Sulfur Pre-existing as Sulfates.—The sample is treated with cold, dilute hydrochloric acid. The filtrate is treated with barium chlorid, the precipitate collected, dried, ignited, to remove organic matter, washed with a mixture of sulfuric and hydrofluoric acids to remove silica, and afterwards weighed as barium sulfate.

Estimation of Sulfur as Sulfids.—Sulfur occurs in this state very seldom and usually reveals its presence by the characteristic order of hydrogen sulfid. The sample is distilled with dilute hydrochloric acid, and the hydrogen sulfid produced is made to pass through an acidulated solution of copper sulfate in such a way

¹⁸ Annales de Chimie et de Physique, 1892, [6], 25 : 305.

Berthelot, Chimie végétale et agricole, Paris, 1899, 4 : 70.

as to transform the sulfur in the hydrogen sulfid into a sulfid, which is afterwards collected and weighed in the usual way. The use of a titrated solution of iodine is not advisable on account of the organic matter which may be present.

Estimation of Sulfur in Etheral Compounds.—These compounds can be decomposed by boiling with a solution of potash or concentrated hydrochloric acid. The resulting sulfuric acid is precipitated with barium chlorid. Subtract from the sulfates thus obtained those pre-existing as sulfates; the difference represents the sulfur present in ethers.

Estimation of Sulfur in Other More Stable Organic Compounds.—This is estimated indirectly by subtracting from the total sulfur that present as sulfates, sulfids, and ethers.

430. Method of van Bemmelen.—As van Bemmelen¹⁹ observes, the estimation of sulfuric acid in soils presents a number of difficulties. A small part of it can be present as sulfate insoluble in water. In addition to this, there is always some sulfur in the organic bodies present. If the soil is extracted with water then the sulfuric acid can be estimated therein if only a trace of humus substance has gone into solution. On the contrary, if there is much humus substance in solution, and also iron oxid, as is the case when the extraction is made with hydrochloric acid, then both of these must be removed, otherwise the estimation is very inexact. By fusing the residue of the solution with sodium carbonate and a little potassium nitrate the organic substance is destroyed, and after treatment with water the iron oxid is separated. If any sulfur has been dissolved in the organic substance present, this is then oxidized to sulfuric acid. The estimation of the sulfuric acid and of the sulfur, therefore, remains unsatisfactory.

In a sample of clay from Java, which was rich in calcium carbonate, but which contained no basic iron sulfate, there was found the following percentages of sulfuric acid:

Exhausted in the cold with very weak hydrochloric acid, 0.04 per cent; the residue treated in the cold with concentrated hydrochloric acid, the solution evaporated and fused with sodium car-

¹⁹ Die landwirtschaftlichen Versuchs-Stationen, 1890, 37 : 284.

bonate and potassium nitrate, 0.07 per cent; again, the residue treated with aqua regia to oxidize the sulfur, the solution evaporated to dryness, fused with sodium carbonate and potassium nitrate, 0.14 per cent; in all 0.25 per cent. A sample of the same soil treated directly with aqua regia, and then evaporated and fused as above, gave two-tenths per cent sulfuric acid. A sample of the same soil ignited in a crucible with sodium carbonate and potassium nitrate gave 0.16 per cent of sulfuric acid. The difference between 0.04 and 0.07 per cent can be attributed to the sulfur in the organic substance which was dissolved by the concentrated hydrochloric acid; the quantity, however, is too small to draw any safe conclusion. Possibly it might have been that the very dilute hydrochloric acid did not dissolve all of the sulfate. The quantity of sulfur combined in the organic substance in the above soil may be derived from the following equation; *viz.*,

$$\frac{0.2 - 0.07}{80} \times 32 = 0.05 \text{ per cent. of sulfur.}$$

The estimation of the sulfur in a sample of soil from Deli was carried on with still greater exactness by three different methods.

The quantities of hydrochloric acid, nitric acid, and sodium carbonate employed were measured or weighed, and the minute content of sulfuric acid therein estimated and subtracted from the final results. The methods employed were as follows:

(A) Extraction with water and afterwards with very dilute hydrochloric acid.

(B) Extraction with cold hydrochloric acid, one part to three of water.

(C) Extraction with aqua regia.

(D) Ignition with sodium carbonate and potassium nitrate.

(E) Ignition in a combustion tube with sodium carbonate in a stream of oxygen.

The percentages of sulfuric acid obtained by the different methods were as follows:

	Per cent.
(A)	0.058
(B)	0.070
(C)	0.140
(D)	0.125
(E)	0.106

431. Method of the Italian Chemists.—The determination of the sulfuric acid present as sulfates, is conducted as follows by the Italian chemists: The soil is completely extracted by diluted hydrochloric acid and the sulfuric acid precipitated in the solution with barium chlorid. If a soil is very rich in calcium sulfate it should first be treated with a warm solution of sodium carbonate to decompose the calcium sulfate, and the sulfuric acid be determined in the solution after having added hydrochloric acid.

432. Estimation of the Chlorin.—The estimation of the chlorin is of great importance in certain cases. When this element is lacking in the soil, which, however, is rare, certain plants appear to suffer from its absence. The quality of the forage plants in particular is influenced by it; but when the chlorids are too abundant, which is a frequent case, they prevent or arrest completely the progress of vegetation. Salty soils are, in general, completely sterile. In the proportion of one pound in a thousand in the earth, sodium chlorid is to be regarded as injurious. It is necessary, therefore, in analysis to take account of two cases; *viz.*, those of soils poor in chlorids and those of soils rich in chlorids.

For soils poor in chlorids the French method directs that²⁰ 200 grams of the earth are to be washed on a filter with boiling water. The liquor is evaporated to dryness and gently heated to a temperature inferior to redness in order to destroy the organic matter. The residue is taken up by small quantities of water and to the filtered liquor the volume of which should not exceed from 40 to 50 cubic centimeters are added ten cubic centimeters of pure nitric acid and a sufficient quantity of silver nitrate to produce a complete precipitation. The precipitate is vigorously shaken and allowed to stand for a few hours in a warm darkened locality. The precipitate is collected upon a double filter and the silver chlorid, after proper desiccation, is weighed.

When the soil is rich in chlorids it is washed as has just been described upon a filter. The wash-waters are made up to one liter and 50 cubic centimeters, equivalent to ten grams of the soil, are used for analysis. This quantity is treated exactly as described above.

²⁰ *Annales de la Science agronomique*, 8th year, 1891, 1 : 289.

433. Wolff's Method of Estimating Chlorin in Soils.²¹—Three hundred grams of the soil are treated with 900 cubic centimeters of pure water containing a little nitric acid, with frequent shaking, and allowed to stand 48 hours. Four hundred and fifty cubic centimeters are filtered and the clear liquid evaporated to 200 cubic centimeters. The chlorin is precipitated with silver nitrate. The quantity obtained, corresponds to that found in 150 grams of the air-dried soil.

A second method, Mohr's, as described by Wolff, is as follows: Fifty grams of the soil are placed in a platinum dish and moistened with a concentrated solution of potassium nitrate, free from chlorin. The mass is evaporated to dryness and gradually heated to a red heat. After cooling it is moistened with water and washed into a beaker and the solid mass quickly separated. The clear liquid is poured off and the residue again washed with water. The clear liquid obtained is saturated with acetic acid, carefully evaporated to dryness and after solution in water, filtration and the addition of a little nitric acid, the chlorin therein is precipitated by a silver nitrate solution, and the precipitate collected and weighed as usual. It is doubtful if chlorin is found in organic combination in soils. The estimation of chlorin is of great practical importance in soils where its abundance threatens to destroy fertility.

434. Method of Petermann.²²—Chlorin in the soil is estimated at the Gembloux station by digesting 1,000 grams of the sample with two liters of distilled water with frequent shaking for 36 hours. After allowing to stand for 12 hours with the addition of one gram of powdered magnesium sulfate to facilitate the deposition of suspended matter one liter of liquid is siphoned and evaporated in a platinum dish with the addition of a few drops of a solution of potassium carbonate free from chlorin and nitric acid. The concentrated solution is filtered, washed, and made up to 250 cubic centimeters. To 100 cubic centimeters of the solution add some nitric acid and precipitate the chlorin with silver nitrate. The rest of the solution is reserved for the estimation of nitrate.

²¹ *Zeitschrift für analytische Chemie*, 1864, 8 : 105.

²² *L'Analyse du Sol*, Brussels, 1891 : 17.

435. Estimation of Silicic Acid.—*Direct Estimation.*—The sample of soil in the method of Berthelot and André²³ is mixed with two or three times its weight of pure sodium carbonate and fused in a silver crucible until complete decomposition has taken place. The residue is dissolved in water and dilute hydrochloric acid. The silicates are decomposed by this treatment and the solution is evaporated to dryness on the water-bath, and when dry slightly heated. The silicic acid (silica) is by this treatment rendered insoluble. It is collected on a filter, washed, ignited, and weighed. The resulting compound is apt to contain some alkalies and should be mixed with ammonium fluorid and sulfuric acid, and after the disappearance of the silica the residue should be dried and weighed. The loss in weight represents the true silica. The loss in weight should be corrected by calculating the sulfates of the alkalies back to oxids. This correction can be neglected when the work has been carefully done, and the washing of the original silica has been well performed.

Indirect Estimation.—The total silica may be estimated indirectly by subtracting from the total weight of the sample the sum of the weights of the other constituents resulting from the separate estimation of each of them after decomposing the sample with hydrofluoric acid.

436. Estimation of Titanium.—The principle of this method rests on the oxidation of a titanium soluble salt with hydrogen peroxid, giving a yellow or red color of greater or less intensity proportional to the quantity of the titanium salt present.²⁴

The powdered soil is fused with sodium acid sulfate, the melt after cooling, exhausted with cold water, filtered, the filtrate brought to a given volume and treated with hydrogen peroxid. The yellow color thus produced is compared with tints secured with known quantities of pure titanium salts.

²³ *Annales de Chimie et de Physique*, 1892, [6], **25** : 308.

²⁴ A. Waller, *Berichte der deutschen chemischen Gesellschaft*, 1882, **15** : 2592.

Preseuius, *Quantitative Chemical Analysis*, 1904, **2** : 1149.

Dunnington, *Journal American Chemical Society*, 1891, **13** : 210.

McCaleb, *American Chemical Journal*, 1889, **10** : 36.

Bain, *Journal American Chemical Society*, 1903, **25** : 1073.

Pellet and Fribourg, *Annales de Chimie analytique*, 1905, **10** : 413.

Previous to fusion the sample may be advantageously treated with hydrochloric and sulfuric acids.

To determine the titanium in the hydrochloric solution of a soil the following method as modified by Walker in the Bureau of Chemistry is used:

An aliquot part of the hydrochloric acid extract is mixed with five cubic centimeters of strong sulfuric acid and heated in a platinum dish until all hydrochloric acid is driven off and the sulfuric acid begins to decompose. After cooling, water is cautiously added to bring the volume up to about 50 cubic centimeters. The solution is then again cooled to room temperature, five cubic centimeters of three per cent hydrogen peroxid solution added, and the volume made up to 100 cubic centimeters with water. A standard solution of titanium is diluted with five per cent sulfuric acid, treated with five cubic centimeters of three per cent hydrogen peroxid, and brought to 100 cubic centimeters with five per cent sulfuric acid. The two colored solutions are allowed to stand for about three minutes and the depth of color then compared, preferably in a colorimetric camera.

Example: The hydrochloric acid extract from ten grams of soil is made up to 250 cubic centimeters. Ten cubic centimeters of this (corresponding to 0.4 gram soil) is treated as above. Five cubic centimeters of a standard solution of titanium, one cubic centimeter of which corresponds to 0.0002 gram TiO_2 , are used. The colors of the two solutions are compared in nessler tubes. Fifty cubic centimeters of the colored soil solution correspond to 26 cubic centimeters of the standard. The 100 cubic centimeters then correspond to 52 cubic centimeters of the standard, which contains 0.00052 gram TiO_2 .

$$\begin{aligned}\text{Then,} \quad & 0.4 : 0.00052 = 100 : x. \\ & x = 0.13 \text{ per cent } \text{TiO}_2.\end{aligned}$$

The standard titanium solution is best made from a pure solution of titanium sulfate dissolved in five per cent sulfuric acid. This stock titanium sulfate solution may be easily prepared by precipitating titanium hydrate from a solution of titanium chlorid or nitrate with ammonia, and dissolving the hydrate in sulfuric acid. The solution may be standardized by evaporating a measured volume to dryness, igniting the residue, and weighing the resulting TiO_2 .

436 (bis.). Simultaneous Estimation of Different Elements.—

The operations and processes for the estimation of each of the elements have been described, but it is often best to carry on an operation in such a way as to gain time by making a single decomposition upon a quantity of soil of some considerable magnitude, and using the results of the solution for the determination of the different substances. From the operations already described it will be easy to make a combination of methods by which all or nearly all the important constituents in a soil may be determined in a single sample. Of the various methods proposed, that of the committee of the French agricultural chemists may be taken as a type.²⁵ In the case of the estimation of lime, potash, magnesia, and sulfuric acid, in which the operation is carried on in a soil which is not incinerated, time may be saved by digesting a considerable quantity of the soil with concentrated nitric acid for a period of five hours. It is best to operate on 100 grams of the soil and increase proportionally the nitric acid. The filtrate, after washing, is made up to one liter and thoroughly shaken. From this amount of liquid, portions are used corresponding to the weights of soil upon which the operation for the determination of each of the constituents would be conducted. For example, for the estimation of lime in the case of a very calcareous earth, ten cubic centimeters representing one gram of the original sample, in the case of a soil poor in carbonates 100 cubic centimeters representing ten grams, and for the estimation of potash, magnesia, and sulfuric acid 200 cubic centimeters, representing 20 grams of the soil, should be used. This method avoids frequent weighings of the earth and separate treatments thereof by the acid.

On the other hand, in the same portion of the solution, the different elements can be estimated. For example, for the estimation of the potash as has been indicated, in the place of precipitating as a whole the sulfuric acid, lime, etc., and of afterwards separating the magnesia in the sole aim of eliminating these bodies, they can be collected separately and weighed, thus securing at a single operation several determinations.

²⁵ *Annales de la Science agronomique*, 8th year, 1891, 1 : 290.

At the beginning some barium chlorid is added and if the barium sulfate is then collected and weighed, the estimation of the sulfuric acid is effected. To the filtrate there are afterwards added some ammonia and ammonium carbonate to precipitate, at once, the excess of barium, the iron and aluminum hydroxids, the lime and the phosphoric acid. This separation being effected the filtrate contains still the magnesia and the alkalies. The first can be separated by means of oxalic acid, collected, and weighed. Finally the potash itself can be estimated in the state of perchlorate or platinochlorid. It has thus been possible in the same suite of operations to estimate in a given quantity of the liquid, the sulfuric acid, the magnesia, the lime, and the potash.

437. Estimation of Kaolin in Soils.—True kaolin is a hydrated aluminum silicate, having the formula $H_4Al_2Si_2O_9$. This substance is, even in concentrated hydrochloric acid, almost completely insoluble. If heated to low redness until its water of constitution is driven off it becomes soluble even in dilute acid. It contains, theoretically, 13.94 per cent of water of combination. The following methods, due to Sachsse and Becker,²⁶ can be used for its determination.

Estimation of the Water of Combination.—Heat from one to two grams of kaolin, dried at 100° , for half an hour in a covered platinum crucible to a temperature which shows an incipient red heat when the crucible is partly protected from the daylight with the hand. This treatment does not quite give the whole of the water of combination but nearly all of it. A kaolin is changed by this treatment into a substance which is easily soluble in dilute hydrochloric acid.

Estimation of the Kaolin in Impure Kaolins.—Mineral kaolin, or the kaolin obtained by silt analysis, is dried at 100° to constant weight. It is then treated with dilute hydrochloric acid until all matters which will pass into solution have been dissolved. The residual kaolin is then washed thoroughly with water and ignited for half an hour at a low red heat. The residual mass is a second time extracted with hydrochloric acid until the silicate no longer passes into solution. The soluble silica and alumina are then esti-

²⁶ Die landwirtschaftlichen Versuchs-Stationen, 1892, 40 : 245 et seq.

mated in the usual way and calculated to kaolin. The result will give the pure kaolin in the sample examined.

The estimation may also be made as follows: Two samples of the impure kaolin are dried to constant weight at 100°. One is extracted with hydrochloric acid in the manner described above and the amount of silica determined. The second is treated directly by ignition to low redness for half an hour, dissolved in hydrochloric acid and the amount of silica determined. The difference in the two percentages of silica corresponds to the silica equivalent to the pure kaolin.

Statement of Results.—It is convenient to incorporate the data obtained by the above methods with the complete mass analysis of the silicate examined. In the sample given below the analysis was made on a clay silt obtained with a velocity of two-tenths millimeter per second.

The mass analysis gave the following data:

Loss on ignition.....	10.04
SiO ₂	51.52
Al ₂ O ₃	17.93
Fe ₂ O ₃	7.42
CaO.....	1.57
MgO.....	6.27
K ₂ O.....	4.1
Na ₂ O.....	1.61

The loss on ignition was made up of the combined water and a trace of humus. On gentle ignition only 7.52 per cent of water came off.

The examination of the non-ignited and the gently ignited silica by means of dilute hydrochloric acid, gave the following data:

	Non-ignited.	Gently ignited.	Difference.
Water.....	10.04	10.04
Insoluble residue.....	40.	34.54	-5.46
Al ₂ O ₃	9.04	10.	+0.96
Fe ₂ O ₃	5.96	7.27	+1.31
SiO ₂	25.27	28.	+2.73
Alkalies and alkaline earths..	9.69	10.15	+0.46

By comparison of these data with those obtained by the mass analysis, the following representation of the distribution of the various components in the clay is obtained:

23.52 per cent SiO_2 in the form of quartz and undecomposed silicates:

2.93 per cent SiO_2 in the form of kaolin:

25.27 per cent in the form of easily decomposable silicates and of the hydrates of SiO_2 :

7.93 per cent Al_2O_3 in the form of undecomposed silicates:

0.96 per cent Al_2O_3 in the form of kaolin:

9.04 per cent Al_2O_3 in the form of easily decomposed silicates and of hydrates:

0.15 per cent Fe_2O_3 in the form of undecomposed silicates:

1.31 per cent Fe_2O_3 in the form of kaolin:

5.96 per cent Fe_2O_3 in the form of easily decomposable silicates and hydrates:

3.55 per cent of alkalies and alkaline earths in the form of undecomposed silicates:

10.00 per cent of alkalies and alkaline earths in the form of easily decomposable silicates:

10.40 per cent of water, including a trace of humus:

Collecting these results the following statement is obtained.

The clay analyzed contained:

10.04 per cent of water, a trace of humus:

35.15 per cent of undecomposed silicates and quartz:

5.00 per cent of kaolin:

50.27 per cent of easily decomposable silicates, hydrates of SiO_2 and hydroxids. These data show an excess of 0.46 per cent over the theoretical composition of the kaolin.

ESTIMATION OF NITROGEN IN SOILS.

438. Introductory Considerations.—The great economic and biologic value of nitrogen as a plant food renders its estimation in soils of especial importance. It is necessary, first of all, to remember that the nitrogen present in soils may be found in four forms; *viz.*, first, in organic compounds, second, as ammonia, third, as nitric or nitrous acid, and fourth, as amido compounds. Further than this each of these classes of nitrogen may be subdivided. The organic nitrogen may be in a form easily nitrified and rendered available for plant food, or it may be inert and re-

sistant to nitrification, as in hair, or exist in an amid state. The ammoniacal nitrogen may exist in small quantities as gaseous ammonia, or be combined with mineral or organic acids. As nitric or nitrous acid the nitrogen will be found combined with bases, or perhaps in minute quantities as free acid, in passing under the influence of the nitrifying ferment from the organic to the inorganic state. To the latter state it must finally come before it is suited to absorption by plants. The amido compounds may also exist in various combinations.

In general, far the largest part of soil nitrogen, excluding the atmosphere diffused in the pores of the soil, is found in the organic state and is derived from the debris of animal and vegetable life and from added fertilizers. As ammonia, the nitrogen can only be regarded as in a transition state, arising from the processes of decay, or incomplete nitrification. As nitric acid, it is found as a completed product of nitrification, or as the result of electrical action. The processes of nitrification and the isolation and determination of the nitrifying organisms are problems intimately related to the subject of fertilizers and will be considered in the second volume of this manual. By reason of the great solubility of the nitrates, and the inability of the soil to retain them in the presence of an excess of water, there can never be a great accumulation of nitric acid in the soil save in localities deficient in rain-fall or in specially protected spots, such as caves. Moreover, there is no part of the soil which has any special power of holding back nitric acid as it passes in aqueous solution through its pores. The nitric acid, therefore, produced in the soil passes at once into growing vegetation, remains in store in dry periods, or is found eventually in the drainage waters.

Under the teachings of the earlier theories of oxidation, the formation of ammonia in soil containing much vegetable matter is thought by Berthelot and André²⁷ to be due to the progressive decomposition of amid principles under the influence of dilute acids or alkalis, either in the cold or at an elevated temperature or under the influence of pure water at ordinary temperatures. Soils of the above description, of themselves, contain neither free

²⁷ Bulletin de la Société chimique de Paris, 1891, [3], 5 : 643.

ammonia nor ammoniacal salts, and the ammonia which is found in the analysis of these soils comes from the reaction above indicated. The ammonia which is found in these soils, as well as that given off to the surrounding atmosphere, comes from the same class of decompositions, and these decompositions, in this case, are effected by the water itself, or by the alkaline carbonates of the soil. The amid principles which are thus decomposed belong either to the class of amids proper, derived by the displacement of hydrogen in ammonia by acids, or to the class of alkalamids derived from nitrogenous bases, both volatile and fixed. Among these alkalamids some are soluble in water and some insoluble, and the decomposition of these last by acids or by alkalies may furnish bodies which themselves are either soluble or insoluble in water.

To determine the nature of the nitrogenous principles in a soil rather rich in humus, Berthelot and André apply the following treatment:

A soil containing 19.1 grams of carbon and 1.67 grams of nitrogen per kilogram is first subjected to treatment, at room temperature, with a concentrated solution of potash. By this treatment 17.4 per cent of the nitrogen content is set free under the form of ammonia. One-quarter of this is obtained during the first three days; one-eighth during the next three days. Afterward the action becomes much more feeble and when continued during 40 days longer, the evolution of the gas is diminished almost proportionately to the time. It appears from the above observations that the amid principles of the soil, decomposable by potash, belong to two distinct groups, which are broken up with very unequal velocities. The soil, treated on the water-bath for 13 hours at 100° with strong potash, shows the following behavior in respect to its nitrogenous constituents: Nitrogen eliminated in the form of ammonia, 16 per cent; nitrogen remaining in the part soluble in potash, ten per cent; nitrogen remaining in the part insoluble in potash 74 per cent.

Treatment with Acid.—The insoluble nitrogenous compounds of the soil are also decomposed by dilute acids, and often more rapidly than by the alkalies. The method of treatment is substantially the same as that set forth above. The decompositions

effected either by alkalies or by acids tend in general to lower the molecular weights of the resulting products. The prolonged action of alkalies at the temperature of boiling water rendered soluble, after 26 hours of treatment, 93.6 per cent of the organic nitrogen found in the vegetable mould. By treating the earth successively with alkalies and acids 95.5 per cent of the total nitrogen were decomposed. These experiments show how the insoluble nitrogen in humic compounds can be gradually rendered assimilable. The action of vegetables is not assuredly identical with those which acids and alkalies exercise. However, both present certain degrees of comparison from the point of view of the mechanisms set in play by the earthy carbonates and carbon dioxide, as well as by the acids formed by vegetation. The reactions which take place naturally, while they are not so violent as those produced in the laboratory, make up by their duration what they lack in intensity.

For a more detailed study of the nature of the nitrogenous elements in soil the following method of treatment, due to Berthelot and André, is recommended:

Treatment of the Soil with Alkalies.—1. Reaction with cold, dilute solution of potash: Mix 50 grams of the sample, dried at 110° , with a large excess of ten per cent potash solution and place under a bell-jar containing standard sulfuric acid. The mixture is left for a long time in order to secure as fully as possible the ammonia set free.

Example: Fifty grams of a soil contained 0.0814 gram of nitrogen. Treated as above it gave the following quantities of nitrogen as ammonia:

		Nitrogen as Ammonia.
After 3 days.....		0.0034 gram
" 6 "	0.0054 "
" 11 "	0.0065 "
" 17 "	0.0078 "
" 25 "	0.0093 "
" 41 "	0.0107 "
" 46 "	0.0141 "

It is seen that the action still continued after 40 days. In the space of 40 days 17.4 per cent of the total nitrogen contained in

the soil had been converted into ammonia by dilute potash. According to the above observations the amid principles transformed into ammonia under the influence of dilute potash, exist in groups which are acted on with very unequal rapidity.

2. Reaction with hot dilute solution of potash: Mix 200 grams of the soil sample, with one and one-half liters of dilute potash solution containing 50 grams of potash. Place in a flask and heat on a boiling water-bath for six hours. The flask is furnished with a stopper and tubes, and a current of pure hydrogen is made to pass through the liquid, having the double object of preventing any oxidizing effect from the air and of carrying away the ammonia which may be formed. The escaping hydrogen and ammonia are passed into a bulb apparatus containing titrated sulfuric acid.

The sample of soil employed contained in 200 grams, 0.3256 gram of nitrogen. There was obtained at the end of six hours' heating, 0.0366 gram of nitrogen. In other words, 11.24 per cent of the total nitrogen in the sample appeared as ammonia.

Examination of Residue.—After the separation as ammonia as above described, pour the residue in the flask on a filter, wash with hot water, and determine nitrogen in the filtrate and in the solid matter on the filter by combustion with soda-lime. The filtrate is, of course, first evaporated to dryness after being neutralized with sulfuric acid.

The insoluble part contained 0.041 gram of nitrogen, *i. e.*, 12.84 per cent of the entire amount.

The soluble part contained 0.2411 gram of nitrogen, *i. e.*, 74.05 per cent of the whole.

Summary of Data.—In the sample analyzed the following data were obtained:

	Of the whole.
Nitrogen as ammonia.....	11.24 per cent.
“ in insoluble part.....	12.84 “ “
“ in soluble part.....	74.05 “ “
“ not determined.....	1.87 “ “
Sum.....	100.00 “ “

The same experiment in which the heating on the water-bath was continued for 13 hours gave the following data:

	Of the whole.
Nitrogen as ammonia.....	16.02 per cent.
“ in insoluble part.....	9.98 “ “
“ in soluble part.....	74.00 “ “
Sum.....	100.00 “ “

Further Treatment of Matter Insoluble in Hot Dilute Potash.—

A portion of the insoluble portion from the last experiment is treated for 13 hours longer under the same conditions with dilute hot potash. The soluble and insoluble portions are determined as already described. Of the nitrogen insoluble after 13 hours, 64.21 per cent remained insoluble after the second 13 hours. This fact shows that a slow and progressive decomposition of the alkalamids in the soil occurs under the influence of hot dilute potash.

Treatment of Matter Insoluble in Hot Dilute Potash with Hydrochloric Acid.—A part of the material insoluble in hot potash after 13 hours is mixed with dilute hydrochloric acid, in such proportion as to have one-fifth the weight of pure hydrochloric acid to the dry solid matter. Heat in flask on a boiling water-bath for 13 hours and determine the nitrogen in the insoluble residue.

Example: In the case given it was found that 54.91 per cent of the nitrogen insoluble in dilute hot potash were dissolved by the hot hydrochloric acid.

This fact shows that insoluble nitrogen compounds contained in the soil are dissolved by dilute acids even more readily than by dilute alkalies at the temperature of boiling water.

Several reactions appear to take place simultaneously when potash is brought into contact with the nitrogenous principles of arable earth. Some of these principles, during the first period of the action become soluble and even form compounds which are not precipitable by acids. When, however, the action of the potash is prolonged, the dissolved bodies lose little by little a part of their nitrogen as ammonia or as soluble alkalamids. They become thus changed either to compounds no longer soluble in the potash, or to those insoluble in the solution when acidified. These compounds, it is true, contain nitrogen, but are poorer in this element and have a higher molecular weight, or, in other words, are condensation products. These last bodies are not absolutely stable

in the presence of potash, but are decomposed much more slowly than the original bodies from which they were derived.

In general, it may be said that under the influence of alkalis on the nitrogenous principles of the soil there is a tendency to form two classes of bodies, the one more soluble with a lower molecular weight, the other less soluble with a higher molecular weight. The inverse relation between solubility and condensation is in agreement with what is observed in similar reactions with organic bodies in general. It certainly plays an important rôle in the transformations which an arable soil undergoes, either through the mild influences of the air and natural waters, or the more energetic action of vegetables themselves.

The methods of estimating nitric nitrogen will be made the theme of a special study in connection with the chapter on nitrification in the second volume of this manual. There will be considered here, therefore, the methods of determining organic and ammoniacal nitrogen in the soil with only such incidental treatment of the methods for nitric nitrogen as the processes applicable to the other forms may contain.

439. Earlier Methods of the Association of Official Agricultural Chemists.²⁸—The nitrogen compounds in the soil are usually placed in three classes.

1. The nitrogen combined with oxygen as nitrates, or nitrites, existing as soluble salts in the soil.
2. The nitrogen combined with hydrogen as ammonia, or organic nitrogen easily convertible into ammonia. The ammonia may exist as salts, or may be occluded by hydrated ferric or aluminum oxids and organic matter in the soil.
3. The inert nitrogen of the soil or the humus nitrogen.

Active Soil Nitrogen.—The material proposed for reducing the nitrates to ammonia, and at the same time to bring ammonia salts and organic nitrogen into a condition for separation by distillation, is sodium amalgam. Liquid sodium amalgam may be readily prepared by placing 100 cubic centimeters of mercury in a flask of half a liter capacity, covering the warmed mercury with melted paraffin, and dropping into the flask at short intervals pieces of

²⁸ Bulletin No. 38, Division of Chemistry : 204.

metallic sodium, the size of a large pea, taking care that the violence of the reaction does not project the contents from the flask, till 6.75 grams of sodium have combined with the mercury. The amalgam contains one-half per cent of sodium and may be preserved indefinitely under the covering of paraffin. To estimate the active soil nitrogen, place 50 grams of air-dried soil in a clean mortar, add 200 cubic centimeters of ammonia-free distilled water, rub up the soil with a part of the water to a smooth paste, transfer this to a flask of one liter capacity, washing the last traces of the soil into the flask with the rest of the water: Add 25 cubic centimeters of the liquid sodium amalgam and shake the flask so as to break the sodium amalgam into small globules distributed through the soil. Insert a stopper with a valve and set aside in a cool place for 24 hours. Pour into the flask 50 cubic centimeters of milk of lime, and distill, on a sand-bath, 100 cubic centimeters into a flask containing 20 cubic centimeters of decinormal sulfuric acid, and titrate with decinormal soda solution, using dimethyl-orange as indicator. Estimate the nitrogen of the ammonia found as active soil nitrogen.

If the ammonia produced is too small in amount to be readily estimated volumetrically, determine it by nesslerizing the distillate.

Estimation of Nitrates in the Soil.—When it is desired to estimate separately the nitrates in the soil, the following method may be used: Extract the nitrates with water, evaporate 100 cubic centimeters of the soil extract to dryness on the water-bath, dissolve the soluble portion of the residue in 100 cubic centimeters of ammonia-free distilled water, filtering out any insoluble residue, place the solution in a flask and add ten cubic centimeters of liquid sodium amalgam, insert stopper with valve, set it aside to digest in a cool place for 24 hours, add 50 cubic centimeters of milk of lime, distill and titrate as above, and estimate the nitrogen as N_2O_5 .

Nesslerizing may be substituted for titration when the amount of nitrates is small.

An approximate estimation of the amount of nitrates will be of value in determining which method of estimation to use. This may be secured by evaporating a measured quantity of the soil ex-

tract, say five cubic centimeters, on a porcelain crucible cover on a steam-bath or radiator, having first dissolved a minute fragment of pure brucin sulfate in the soil extract. When dry pour over the residue concentrated sulfuric acid, free from nitrates, and observe the color reactions produced. If the nitrate (reckoned as KNO_3) left upon evaporation does not exceed the two-thousandth part of a milligram, only a pink color will be developed by adding the sulfuric acid; with the three-thousandth part of a milligram, a pink with faint reddish lines; with the four-thousandth part, a reddish color; with the five-thousandth part, a red color.

By increasing or diminishing the amount of soil extract evaporated to secure a color reaction of a certain intensity, an approximate estimate may be made of the amount of nitrates present.

Blank experiments to test the acid and the brucin sulfate will be required before confidence can be placed in such estimations.

Total Nitrogen of Soils.—The total nitrogen may be determined by combustion with soda-lime, but this process is often unsatisfactory because of the large amount of material required when the organic matter or humus is small in amount and the process has now little more than historical value.

A modification of the kjeldahl method is more easy to carry out and gives results equally satisfactory. Place 20 grams of soil in a kjeldahl flask, and add 20 cubic centimeters of sulfuric acid (free from ammonia) holding in solution one gram of salicylic acid. If the soil contain much lime or magnesia in the form of carbonate, enough more sulfuric acid must be added to secure a strongly acid condition of the contents of the flask. Add gradually two grams of zinc dust, shaking the contents of the flask to secure intimate mixture. Place the flask in a sand-bath and heat till the acid boils, and maintain the boiling for ten minutes. Add one gram of mercury and continue the boiling for one hour, adding ten cubic centimeters of sulfuric acid if the contents of the flask are likely to become solid. Cool the flask and wash out the soluble materials with 200 cubic centimeters of pure water, leaving the heavy earthy materials. Rinse the residue with 100 cubic centimeters of water, and add this to the first washings. Place this soluble acid extract in a liter digestion flask, add 35 cubic

centimeters of a solution of potassium sulfid, and shake the flask to secure intimate mixture of the contents. Introduce a few fragments of granulated zinc, pour in 75 cubic centimeters of a saturated solution of caustic soda, connect the flask with a condenser and distill 150 cubic centimeters into a flask containing 20 cubic centimeters of acid, using the same acid and alkali for titration used in the kjeldahl method under fertilizers, described in volume second.

Enter the nitrogen found in this operation as total soil nitrogen. The difference between the total soil nitrogen and the active soil nitrogen will express the inert nitrogen of the soil, that is, nitrogen as organic or amido compounds not assimilable by plants without further oxidation.

440. The Official Method.—The procedure for the determination of total soil nitrogen which is now practiced by nearly all American chemists is the official method.²⁹

From seven to 14 grams of the soil, free of nitrates, are placed in a small kjeldahl digesting flask, of about 250 cc. capacity, with 30 cc. of strong sulfuric acid, or more, if necessary, and 0.7 gram of yellow oxid of mercury, and boiled for an hour. The residue is oxidized with potassium permanganate in the usual way. After cooling, the flask is half filled with water, vigorously shaken, the heavy matters allowed to subside, and the supernatant liquid poured into a flask of from 1,000 to 1,200 cubic centimeters capacity. This operation is repeated until the ammonium sulfate is practically all removed and the distillation flask is a little more than half full. The ammonia is distilled in the usual manner. When soils contain any notable quantity of nitrates or nitrites these may first be extracted with water and determined separately and the residual soil treated as above, or the modified gunning method for nitrates described in volume second of this manual be used.

441. Hilgard's Method.³⁰—The humus determination will, in the case of virgin soils, usually indicate approximately the store of nitrogen in the soil, which must be gradually made available by nitrification. Ordinarily (outside of the arid regions) the deter-

²⁹ Bulletin No. 46, Bureau of Chemistry : 76.

³⁰ Bulletin No. 38, Division of Chemistry : 81.

mination of ammonia and nitrates present in the soil is of little interest for general purposes, since these factors will vary with the season and from day to day. Kedzie proposes to estimate the active soil nitrogen (ammonia plus nitrates and nitrites) by treatment of the whole soil with sodium amalgam and distillation with lime. The objection to this process is that the formation of ammonia by the reaction of the alkali and lime upon the humus amids would greatly exaggerate the active nitrogen and lead to a serious overestimate of the soil's immediate resources.

The usual content of nitrogen in black soil-humus is from six to eight per cent in the regions of summer rains. From late determinations it would seem that in the arid regions the usually small amount of humus (often less than two-tenths per cent) is materially compensated by a higher nitrogen percentage. It thus becomes necessary to determine the humus nitrogen directly; and this is easily done by substituting in the grandeau process of humus extraction potash or soda-lye for ammonia water, and determining the nitrogen by the kjeldahl method in the filtrate.

The lye used should have the strength of four per cent in the case of potassium hydroxid, and three per cent in that of sodium hydroxid. The black humus filtrate is carefully neutralized with sulfuric acid, evaporated to a small bulk in a beaker or evaporating basin, and the liquid finally evaporated to dryness in the kjeldahl flask itself by means of a current of air. The beaker or basin is washed either with some of the alkaline lye, or, after evaporation, with warm concentrated sulfuric acid, which is then used in the nitrogen determination in the usual way.

For the determination of nitrates in the soil it is, of course, usually necessary to use large amounts of material, say not less than 100 grams, and, according to circumstances, five or more times that amount. In the evaporated solution the nitric acid is best determined by the reduction method, as ammonia.

Usually the soil filtrate is clear and contains no appreciable amount of organic matter that would interfere with the determination; yet in the case of alkaline soils (impregnated with sodium carbonate) a very dark colored solution may be obtained. In that case the soil may advantageously be mixed with a few per cent

of powdered gypsum before leaching; or the gypsum may be used in the filtrate to discolor it by the decomposition of sodium carbonate and the precipitation of calcium humate. The evaporated filtrate can then be used for the nitrate determination by either the kjeldahl, griess, or the nessler process, which will, of course, include such portions of the ammoniacal salts as may have been leached out. The above named processes will be fully described in the second volume.

For the separate determination of these and of the occluded ammonia, when desired, it is probably best to mix the wetted soil intimately with about ten per cent of magnesium oxid and distill into titrated hydrochloric acid. For general purposes, however, this determination is usually of little interest.

442. Müller's Modified Kjeldahl Method.—Numerous difficulties, as stated by Müller,³¹ have attended the attempts to apply the kjeldahl method for the estimation of nitrogen to samples of soil, and he has modified the method to some extent and made comparisons of the quantity of nitrogen by this modified method and by the soda-lime method.

The principal difficulty encountered by him has been in the regular heating of the mixture of fuming sulfuric acid and soil. The particles of soil are deposited at the bottom of the flask and the result is that the bottom layers become overheated, and, being poor conductors of heat, fail to transmit a sufficient quantity of heat to penetrate to the upper layers of the liquid to complete the reaction. In order to avoid this difficulty Müller heats his flask in a small stove formed with a straight vertical cylinder of iron or copper, the upper end of which is covered with a sheet of iron pierced with a hole which allows the neck of the flask to pass through, while the lower end is closed with a piece of sheet iron furnished on its upper surface with a layer of asbestos. This cylinder of metal is surrounded with a second one, concentric with the first, through which passes a current of heated gases furnished by an ordinary bunsen. By heating the flask in this stove or furnace an even distribution of the heat is secured to all parts of the mixture, but the little drops of sulfuric acid, which are condensed

³¹ *Annales de Chimie et de Physique*, 1891, [6], 22 : 393.

on the cold part of the neck, sometimes lead to the fracture of the glass as they run down the sides of the flask to the hot portions. To prevent the reflux of this condensed acid, which only needs to be done near the end of the reaction, when it is necessary to heat to a very high temperature, the neck of the flask is bent at the point immediately above its emergence at the upper surface of the furnace, so as to dip slightly towards its mouth, and carried into a flask of about 75 cubic centimeters capacity, which will receive the drops of sulfuric acid condensed during the operation. The furnace has the following dimensions; height, 12 centimeters; diameter of interior cylinder, five and one-half centimeters; diameter of exterior cylinder, seven and one-half centimeters.

It is supported on a triangle of large iron wire and is heated by an ordinary bunsen, or by a concentric bunsen, according to the temperature which it is necessary to obtain. The proportions which should be observed between the amount of earth employed and the sulfuric acid are about as follows:

Of the dry earth, 15 grams; of the fuming sulfuric acid, 30 cubic centimeters. There should also be added to the mixture about three-tenths of a gram of pure stearic acid, or better, benzoic acid to aid in converting the organic nitrogen into ammonium sulfate. When the soil to be analyzed does not contain carbonate, the sulfuric acid should be added in two portions. At first add about 20 cubic centimeters of the acid, and after shaking it, the other ten cubic centimeters, running it in from a burette or a pipette in such a manner as to wash thoroughly the neck and sides of the flask. If the earth contain carbonate, however, it is necessary to add the fuming acid in small portions of about five cubic centimeters at a time, waiting each time until the disengagement of the gas caused by the previous addition has ceased. A soil which contains from 30 to 40 per cent of calcium carbonate should be carefully treated in a porcelain capsule with a slight excess of sulfuric acid, pure and dilute. The mixture is afterwards to be evaporated to dryness upon a sand-bath and the residue heated in a drying oven to 110°. The mass is then pulverized, introduced into the flask, treated with three-tenths of a gram of benzoic acid and 30 cubic centimeters of fuming sulfuric acid,

and heated as indicated above. In all cases it is necessary to continue the heating until the contents of the flask are colorless.

With soils containing considerable quantities of iron, however, a slight red color will probably be observed which will not interfere with the accuracy of the tests.

The heating should at first be gentle and the temperature afterward elevated little by little, and finally the heat should be sufficiently great to distill about one and one-half cubic centimeters of sulfuric acid. The operation lasts from 12 to 18 hours. When the reaction is terminated, the cooled mass is taken up with water absolutely free from ammonia, filtered into a flask, and washed upon the filter until the volume of the filtered liquid is about 350 cubic centimeters. Afterward an excess of soda-lye, at 50° Baumé is added, a few pieces of quartz to facilitate boiling, the flask connected with a condenser, the liquid distilled and received in a conical flask closed by a cork having two holes, one of which permits the entrance of the end of the condenser, and the other of a glass tube which is connected with a small flask containing water, the neck of the receiving flask being inclined toward the condenser to avoid the entrainment of any of the alkaline liquid which may be distilled. The distilling flask rests upon two or three pieces of sheet iron, is heated with an ordinary burner, and the ebullition is perfectly regular. From 170 to 180 cubic centimeters of the liquid are distilled in from three and one-half to four hours. The distilled liquid, treated with a few drops of litmus, is titrated by a solution of sulfuric or hydrochloric acid, of which one cubic centimeter corresponds to 0.001 cubic centimeter of nitrogen. The operation both in digestion and distillation appears to be excessively prolonged.

443. Modification of the Kjeldahl Method by Arnold and Wedemeyer.³²—For the oxidizing liquid, a mixture of three grams of benzoic acid with 40 cubic centimeters of H_2SO_4 is employed. After placing the mixture in the digestion flask with the sample of soil, the whole is gently shaken for a few minutes to prevent clotting. The temperature is then raised until acid vapors begin to come off, when one gram of copper sulfate and one gram of

³² Zeitschrift für analytische Chemie, 1892, 31 : 525.

mercuric oxid are added; and after from ten to 15 minutes to avoid foaming, from ten to 20 grams of potassium sulfate are added. The sublimate noticed on the walls of the flask is benzoic acid and does not interfere with the accuracy of the determination.

This method has given good results with the alkaline nitrates, the nitrates of barium, mercury, silver, lead, and with strychnia, ammonia, pyridin, azobenzol, dinitrobenzol, and picric acid.

444. Prevention of Bumping During Distillation.—Daffert has employed the modified kjeldahl method, but found considerable difficulty owing to the violent bumping of the liquid in the distillation. This was especially the case where the sample contained a large proportion of sand. To overcome this annoyance and danger he devised the following process:³³

Fit into the mouth of a large-mouth distillation flask a stopper having two perforations. Through one of the perforations pass the usual distillation tube, through the other a similar tube connected with a supply of steam. Bring the contents to a brisk boil, after which a small current of steam is turned on, and passed in a small stream through the contents of the flask during the distillation. By this means, not only is all danger from bumping avoided, but the time required for the distillation shortened. By the old method it usually requires from 15 to 20 minutes, whereas when the above device is used the distillation requires only from six to ten minutes.

445. Determination of Organic Nitrogen by the Soda-Lime Method.—In the description of the method following, the directions of the French Committee of Agricultural Chemists have been made the base of the analytical process.³⁴ This method is, in this country, almost superseded by the moist combustion process with sulfuric acid. By reason of its long use, however, and because it has been employed by the agricultural chemists of France, Italy, and England, in numerous recorded data, it merits a full description. It is recommended also by Berthelot and

³³ Relatorio annual do Instituto agronomico do Estado São Paulo, (Brazil), 1893, Article XIV : 107.

³⁴ Annales de la Science agronomique, 8th Year, 1 : 253, et seq.

André,³⁵ by the International Congress of Chemists, held in Paris in 1889, by the Italian chemists, and by the official Belgian method,³⁶ in all cases where nitrates are not present in notable quantities. It is only fair to say, however, that these recommendations were made before the kjeldahl process was generally introduced. The nitrogen determinations made in the Division of Chemistry were also conducted by this method for many years before the modern methods of procedure were introduced.

The nitrogen which is found in soils in the organic state is transformed into ammonia when it is heated with soda-lime. This reaction is the base of the process of analysis which has so long been used for this class of bodies. The analytical process is conducted as follows:

A well-cleaned glass combustion tube, closed at one end, is used. The length of the tube is from 35 to 40 centimeters. It is filled first to a depth of two centimeters with calcium oxalate; afterwards to a depth of five centimeters with soda-lime in small fragments; then with the mixture to be analyzed; *viz.*, ten grams of the sample of soil, or 20 grams if poor in nitrogen and organic matters, mixed with soda-lime reduced to a coarse powder. This mixture should occupy a length of about 20 centimeters in the tube. The soil and soda-lime are mixed in a mortar. Afterwards the mortar is rubbed with small quantities of soda-lime, and this, together with the copper boat which has been used in introducing the mixture, is thoroughly washed with the soda-lime, which is poured into the tube until it is filled to within four centimeters of its open extremity. The open end of the tube is closed with a wad of asbestos packed sufficiently tight to prevent the carrying off of the soda-lime by the gas which may be generated during the combustion. The combustion is commenced by heating the tube near the open extremity until it is red and carrying the heat progressively towards the part containing the soil mixed with the soda-lime. An ordinary gas combustion furnace is used and the heat graduated in such a way that the bubbles of gas pass off regularly and not too rapidly. The gas is conducted into

³⁵ *Annales de Chimie et de Physique*, 1892, [6], **25** : 300.

³⁶ Petermann, *L'Analyse du Sol*, Brussels, 1891 : 17.

a bulb tube containing a decinormal standard sulfuric acid colored with litmus. The combustion is continued until the whole of the organic material is decomposed, care being taken not to raise the combustion tube above a low redness in order to avoid its softening. At the end, however, the temperature of the combustion tube is raised to a bright red, and the part containing the calcium oxalate is heated little by little for the purpose of evolving hydrogen, which is used to drive out the last traces of ammonia. After the combustion is completed, and the last traces of ammonia driven out, the standard acid which has received the evolved ammonia is removed, the tube leading to it washed, the wash-water collected with the rest of the liquid and titrated with a standard solution of lime-water, the strength of which has previously been determined against standard sulfuric acid.

446. Preparation of the Standard Sulfuric Acid.—The sulfuric acid to be used in making the standard solutions is previously boiled for half an hour in a platinum dish and allowed to cool in a desiccator. The solution contains 61.25 grams of sulfuric acid in one liter. It is recommended that the flask which holds the sulfuric acid be one which has been used for a long time for holding concentrated sulfuric acid, in order to forestall any action of the alkali in the glass upon the acid after its strength has been determined. The solution before described is of such strength as to have each cubic centimeter equivalent to one milligram of nitrogen.

For the estimation of the nitrogen in the soil a tenth normal solution is used, which is prepared by taking 100 cubic centimeters of the normal solution, described above, and diluting to one liter.

Preparation of the Lime-Water.—From 200 to 300 grams of slaked lime are placed in a closed flask of about five liters capacity. This is filled with water and shaken frequently, and left to deposit the matter in suspension. The water which contains the saline particles which may have been present in the lime is poured off. Fresh water is poured on and the flask shaken from time to time. To use this lime-water the clear part of it is decanted into a flask, avoiding, as much as possible, access to the air. The flask

is closed with a cork carrying two tubes drawn out and bent at a right angle. One of these serves for pouring off the water and the other serves for the entrance of the air, which should be free of carbon dioxid. These two tubes are themselves closed by means of a rubber tube carrying a pinch-cock. The strength of the lime-water is fixed by titration with the decinormal standard sulfuric acid.

Preparation of the Soda-Lime.—Six hundred grams of slaked lime in fine powder are saturated with 300 grams of caustic soda dissolved in 300 cubic centimeters of water. The whole is rubbed into a paste and introduced into a crucible which is heated to redness. The contents of the crucible, still hot, are poured out, and rapidly reduced to fragments in a copper mortar in such a manner as to have the pieces about the size of a pea, and without having too much finely powdered soda-lime mixed with them. While still hot it is placed in a flask and well-stoppered. In order that this reagent should contain no nitrogen it is indispensable to use in its preparation materials which contain no trace of nitrates.

Preparation of the Calcium Oxalate.—In a small copper vessel place 100 grams of oxalic acid and add gradually, bringing it to boiling, enough water to dissolve it. Afterwards place in the solution small portions of slaked lime in a state of powder, constantly testing it until turmeric paper indicates that there is a little lime in excess. It is then evaporated, stirring vigorously on the open fire, and the evaporation is finally finished on a steam-bath. The dried material is placed in a flask and well-stoppered. The oxalic acid which is used in this preparation should be free from every trace of nitrogen.

Preparation of the Litmus Solution.—Five grams of litmus are placed in a flask with a flat bottom. Afterwards a few cubic centimeters of ammonia are added, 25 grams of crystallized sodium carbonate, and ten cubic centimeters of water. This mixture is left to digest for some time, with frequent stirring, at a temperature of from 60° to 80°. The digestion is finished in about four or five days, during which time, at intervals, a few drops of ammonia are added, sufficient to maintain always the ammoniacal odor. At the end of this time 200 cubic centimeters of water are

added and the digestion allowed to continue several days more, still maintaining the solution alkaline with ammonia. A slight excess of hydrochloric acid is added, and the matter which is precipitated is received upon a filter where it is washed several times with cold water and allowed to dry at a low temperature.

For use, from one to two grams of this dry precipitate are dissolved in 100 cubic centimeters of alcohol, and there is thus obtained a litmus solution of extreme sensibility.

447. Treatment of Soil Containing Nitrates.—Nitrates exist in small quantities in all arable soils, except perhaps after prolonged and heavy rains. When treated for nitrogen by the soda-lime method above described, a part of the nitric nitrogen is changed to the state of ammonia, while another part escapes estimation altogether, causing an error in case of soils having much nitrate, which it is important to consider. When the soils contain only small quantities of nitrates, this error is insignificant and does not affect sensibly the results, but in the case of earths rich in nitrates it is necessary first to eliminate them before the determination of the nitrogen by the soda-lime method. The operation is carried on as follows:

Twenty grams of the soil are washed on a small funnel, furnished with a plug of asbestos, with small quantities of pure water, in such a way as to cause from 30 to 40 cubic centimeters of water to pass through. The whole of the nitrate is thus removed. The soil is dried and submitted to analysis by the soda-lime method as just described. There are removed with the nitrate only small traces of organic nitrogen, too small to influence the results of the analysis. If, however, it is desired to remove altogether this slight cause of error, evaporate the washwaters, above described, to two or three cubic centimeters; add a few drops of concentrated solution of ferrous chlorid and as much hydrochloric acid, and boil some minutes in order to drive off, in the state of nitrogen dioxid, all the nitric acid. The residue is evaporated to dryness and contains the traces of organic nitrogen. This is added to the soil which is to be treated by the soda-lime method.

448. Müller's Method.—The determination of nitrogen in the soil by soda-lime is carried on as follows by Müller:³⁷

Fifteen grams of fine earth, dried and mixed with a little sugar, are mixed with 30 grams of soda-lime in powder. The bottom of the combustion tube contains a little moist soda-lime, which is heated at the end of the operation at the same time that a current of pure hydrogen is made to pass through it, and the temperature of the tube is raised, little by little, to a distinct redness. The contents of the receiving bulbs are distilled, after the addition of water and soda, in the same apparatus which served in the estimation of nitrogen, by the kjeldahl method, as described in paragraph 442, the determinations and titrations are made also under the same conditions.

Blank determinations are also made under the same conditions to determine the amount of correction to be made by the two methods. In one case soda-lime, heated with pure sugar, gave 0.0002 gram of nitrogen for a total weight of 55 grams of the soda-lime contained in the tube. The fuming sulfuric acid gave 0.0011 cubic centimeters of ammoniacal nitrogen for the volume of 30 cubic centimeters.

The numbers obtained by the kjeldahl method in general, are lower than those obtained by the soda-lime method when no stearic or benzoic acid is used. The numbers obtained when stearic acid alone was used were sometimes inferior to those obtained by the soda-lime method.

The numbers obtained when benzoic acid is used are, in general, about the same as those obtained by the soda-lime method.

It would seem that the double distillation, outlined above, for the kjeldahl method, would not be required if due care were exercised in the first distillation. This variation, therefore, seems to be unnecessary.

In the soda-lime method, time would be saved by the reception of the ammonia in standard acid, and its titration in the usual way, unless a further purification of the nitrogenous products of the combustion by the final distillation be desired.

³⁷ *Annales de Chimie et de Physique*, 1891, [6], 22 : 398.

449. Volumetric Determination of the Nitrogen.—Instead of separating the nitrates, the total nitrogen in the soil can be determined directly by the classic method of Dumas, which consists in bringing the whole of the nitrogen into a gaseous state and afterwards measuring its volume.

The following method illustrates the general principles of the determination:

A glass combustion tube closed at one end, about one meter in length, is selected. In the bottom of this tube is placed some potassium bicarbonate in a crystalline form, in small pieces, filling the tube to a distance of about 20 centimeters. Afterwards copper oxid is placed to the depth of ten centimeters and finally a mixture of from 20 to 30 grams of the earth with from 30 to 40 grams of copper oxid in a fine state of subdivision, and about ten grams of metallic copper obtained by reducing the copper oxid by hydrogen. Next the tube is filled with copper oxid to a depth of from 20 to 25 centimeters, and afterwards with reduced copper to the depth of at least 25 centimeters, and after this another layer of copper oxid of about five centimeters, and finally a plug of asbestos. The combustion tube is closed with a stopper carrying a glass tube of about 90 centimeters in length, of which the extremity, bent into the form of a U, extends to a mercury trough. The glass combustion tube is surrounded with brass gauze, except that part which contains the potassium bicarbonate. The beginning of the operation consists in heating the tube to decompose a part of the potassium bicarbonate, until the whole of the apparatus is filled with carbon dioxid. In order to determine that the whole of the air has been expelled and that the apparatus is entirely filled with carbon dioxid, a part of the gas which is disengaged, is received into a jar filled with mercury, in which a little potash-lye has been placed. If the gas is entirely absorbed by the potash, so that there remain only unappreciable particles, the tube can be regarded as completely free of air. When assurance is given that the air is all out of the apparatus, a jar of about 300 cubic centimeters capacity, filled with mercury and containing from 30 to 40 cubic centimeters of a solution of potash of a density of 42° Baumé, is placed over the outlet tube. The combus-

tion is commenced by heating the anterior part of the tube, avoiding the heating of the part containing the earth. When the first part of the tube has reached the red stage the part containing the earth is gradually heated in order to obtain a gentle evolution of gas. The temperature of the tube is carried to redness and the heating gradually carried back toward the closed extremity, but avoiding raising the temperature of the part containing the potassium bicarbonate. The red heat is continued as long as bubbles of gas are discharged into the reservoir. When the evolution of gas has ceased the apparatus is again filled with carbon dioxid for the purpose of driving out the last traces of nitrogen, by heating again the part of the tube containing the potassium bicarbonate. The evolution of the carbon dioxid should be maintained for about 15 minutes. At the end of this time all the nitrogen will be found in the receiving jar. Sometimes a small quantity of nitrogen dioxid is formed incidentally in the operation. After waiting for a quarter of an hour, in order to permit all the carbon dioxid which may have escaped into the reservoir to be completely absorbed, the receiving jar is carried to a water-basin and the mercury allowed gradually to escape; its place being taken by the water. The gas is then transferred into an azotometer where its volume and temperature are read in the usual way.

In order to absorb any nitrogen dioxid which may be admixed with the nitrogen itself, a little crystal of ferrous sulfate is introduced. The reservoir containing the nitrogen is carried to the mercury trough, and the water which it contains is nearly all run out in such a way as to be replaced with mercury, great care being exercised to avoid any escape of gas. Afterwards there is introduced over the mercury a crystal of ferrous sulfate and the azotometer is shaken until this crystal is dissolved by the water which it still contains. It is then allowed to remain for 20 hours. At the end of this time the nitrogen dioxid is absorbed and the volume of the gas is again read as before. One-half only of the total loss should be subtracted, since the volume of the nitrogen dioxid is twice the volume of the nitrogen itself. For the practice of this method, in connection with the use of a mercury pump, the directions which will be given under fertilizers in volume second, may be consulted.

450. Estimation of Ammonia.—Ammonia exists ordinarily only in very small quantities in the soil, since it is incessantly transformed into nitrate or diffused in the air. Nevertheless, it is sometimes interesting to determine its quantity. It is rarely found in a free state, but in combination with carbonic acid the humic acids or other free acids in the soil.

The method of determining the ammonia in soils is one of extreme delicacy on account of the small proportion therein, and the difficulty of expelling it without at the same time converting some of the organic nitrogen into ammoniacal compounds. The various methods employed for this purpose may be classified as follows:

1. Treatment of the soil with soda-lye in the cold, and the absorption of the ammonia given off by standard sulfuric acid.
2. The method of Boussingault, which consists in replacing the soda-lye with magnesia and distilling the ammonia at a boiling temperature, absorbing the distillate in a standard acid.
3. A modification of the above method, due to Schlösing, which consists first in extracting the ammonia by hydrochloric acid and subjecting the extract to distillation with magnesia.
4. The method of Knop consists in treating the soil in a closed cylinder with soda-lye containing bromin. The ammonia set free by the lye is decomposed in the presence of bromin into free nitrogen and hydrobromic acid. The nitrogen is collected and measured in an azotometer. The brom-soda-lye is prepared by dissolving 100 grams of sodium hydroxid in 1,200 cubic centimeters of water and adding 25 cubic centimeters of bromin.

5. The process described under 4, as shown by Baumann,³⁸ does not give accurate results and it has been modified by him as follows: Two hundred grams of soil are treated with 100 cubic centimeters of dilute hydrochloric acid (one part acid and four of water) free of ammonia; 300 cubic centimeters of ammonia-free distilled water are added and digested for two hours with frequent stirring. If a soil contain much calcium carbonate larger quantities of acid must be used. Two hundred cubic centimeters of the filtrate are placed in an evolution flask, connected with an

³⁸ Die landwirtschaftlichen Versuchs-Stationen, 1886, 33 : 247 et seq.

azotometer, with five grams of freshly burned magnesia. The flask is fitted with a stopper carrying two glass tubes, one of which reaches to the bottom and serves to introduce the ozone. The mixture is then oxidized as follows: Ozone is generated by adding three parts by weight of sulfuric acid to one part of dry and powdered potassium permanganate. A stream of air is drawn through the ozone generator by an aspirator, and the ozone is conducted into the flask containing the hydrochloric acid extract of the soil and magnesia. The oxidation is completed in about ten minutes. The mixture is then brought into the azotometer and the nitrogen set free and measured in the usual way.

It has been shown that if asparagin or glutamin be present in the soil they are decomposed by the soda-lye and the results obtained are too high. It has been further proved that soils which contain a notable quantity of humus give, with soda-lye in the cold, a practically continuous evolution of ammonia. Moreover, soils which are rich in humus and which have been treated by distillation with magnesia give, on subsequent treatment with soda-lye, considerable additional quantities of ammonia.

Comparison of Methods of Estimating Ammonia.—Baumann has determined the ammonia-nitrogen in various soils by the soda-lime method, distillation of the hydrochloric acid extract with magnesia, and the azotometric method modified as indicated above. These methods will be designated as 1, 2, 3, respectively in the following table.

No. of sample.	METHOD.		
	1.	2.	3.
	Ammonia-nitrogen in one kilogram of soil.		
	Gram.	Gram.	Gram.
1	0.0448	0.02227	0.02781
2	0.0168	0.01105	0.01326
3	0.0336	0.01771	0.02212
4	0.0056	0.00443	0.00443
5	0.0280	0.02337	0.02894
6	0.0196	0.01243	0.01672

From the above figures it is seen that the method usually attributed to Schlösing gives uniformly higher numbers than either of the other processes, while the third gives slightly higher values than the second.

451. The Magnesia Distillation Process.—If a sample of soil be

distilled directly with magnesia and water, there is danger on the one side of not extracting all the ammonia, by reason of the absorbing power of these bodies, and on the other, of transforming into ammonia the nitrogen of the organic matters. It is therefore preferable to separate the ammonia from the soil in the form of chlorid, and to subject this extract to distillation.

In a small sample of the soil the humidity is determined by drying at 100° until there is no further loss of weight. The quantity of moisture being known, 200 grams of air-dry soil are moistened with water, and then there is added, in small portions, some dilute hydrochloric acid, shaking frequently until the whole of the calcium carbonate present is decomposed. The liquor should remain acid at the end of the operation, but without containing a notable excess of acidity. Knowing beforehand the quantity of moisture contained in the 200 grams, water is added until the total quantity shall be equal to 500 cubic centimeters. The whole is then shaken and allowed to repose, filtered rapidly, covering the funnel with a glass vessel and receiving the liquid which runs through in a flask with a narrow opening. Two hundred and fifty cubic centimeters of this liquor, or mixture, represent 100 grams of earth of known humidity. This quantity is introduced into a flask for determining the ammonia and five grams of calcined magnesia added. Before commencing the distillation, assurance should be had that the magnesia has completely saturated the acid in excess, and that the liquor is alkaline.

If, by chance, the liquor should be still acid it would be necessary to add sufficient magnesia in order that the reaction should be manifestly alkaline. Afterwards the distillation is begun and the ammonia is received in an appropriate vessel containing one-tenth normal sulfuric acid and titrated in the usual way, or, if in minute quantity, nesslerized.

Inasmuch as the quantities of ammonia contained in the soil are generally very small it is necessary to be very particular in order to avoid errors. The distilled water which is employed should be deprived of all traces of ammonia by prolonged ebullition, and the hydrochloric acid should be distilled in the presence of a little sulfuric acid. The treatment with hydrochloric acid is for the

purpose of destroying the absorbing properties of the soil for ammonia, and to permit this last to enter into solution as chlorid. When there is need of very great precision it is convenient to make a blank operation with the hydrochloric acid and water which are employed, in order to make a correction for the traces of ammonia which these reagents may contain.

452. Estimation of Ammoniacal and Amid Nitrogen by the Method of Berthelot and André.³⁹—Heat 100 grams of earth for 13 hours on a steam-bath with about 500 cubic centimeters of dilute hydrochloric acid (15 grams of hydrochloric acid to 500 cubic centimeters of water). At the end of this time throw the contents of the flask on a filter and wash with hot water until the acid reaction has ceased. Determine both the ammoniacal and amid nitrogen in the soluble, and the total nitrogen in the insoluble portion, the ammoniacal by distillation with magnesia, and the amid and total with soda-lime.

Example. A soil contained 0.1669 per cent total nitrogen. Of this there were obtained:

	Per cent.
As ammoniacal nitrogen.....	13.7
In the soluble part as amid nitrogen.....	56.2
In the insoluble part, total nitrogen.....	29.7
Sum.....	99.6

Treatment of the Insoluble Portion.—Treat the part insoluble in hydrochloric acid with a three per cent solution of potash on a steam-bath for 13 hours. Estimate the nitrogen remaining insoluble, from which the part dissolved can be determined by difference. The potash will dissolve usually about two-thirds of the remaining nitrogen.

About 90 per cent of the total nitrogen present in an arable soil will be rendered soluble by successive treatment with acid and alkali. The reverse treatment will give practically the same result. It is therefore immaterial, from an analytical standpoint, whether the acid or alkali be used first.

453. Estimation of Volatile Nitrogenous Compounds Emitted by Arable Soil.—The following method, due to Berthelot and André,⁴⁰ may be practiced:

³⁹ *Annales de Chimie et de Physique*, 1892, [6], 25 : 327.

⁴⁰ *Annales de Chimie et de Physique*, 1892, [6], 25 : 330.

Porcelain pots, containing one kilogram of soil, are placed under bell-jars of 50 liters capacity adjusted to glass dishes designed to receive the waters of condensation.

During the first period the pots are to be sprinkled from time to time, during the duration of the experiment, through the upper tubulature, so as to prevent the soil from becoming dry. The evaporated water is partly condensed on the sides of the bell-jar. It is removed each week through the inferior tubulature, treated with a little dilute sulfuric acid, and preserved for further study. A small vessel containing dilute sulfuric acid is placed under the bell-jar near the porcelain pot for the purpose of collecting, as far as possible, the evolved ammonia.

During the second period the pots are not sprinkled, the soil becomes dry and there is no longer any condensation of water on the walls of the bell-jar. The two periods should include about five months, from May to October.

At the end of the second period the following determinations are to be made:

1. The ammonia absorbed by the dilute sulfuric acid.
2. The ammonia set free by distillation with magnesia, such as may have accumulated in the condensed water.
3. The organic nitrogen contained in the latter after elimination of the ammonia. This is determined by adding a slight excess of acid, evaporation to dryness, and combustion with soda-lime, or by moist combustion with sulfuric acid.

Example:

Earth Employed.—One kilogram of sandy clay containing total nitrogen, 0.09 gram. Nitrogen in sprinkling water, 0.000048 gram.

Nitrogen in Exhaled Products:—

FIRST PERIOD. SPRINKLING.		Gram.
Ammoniacal nitrogen collected in the dilute sulfuric acid		0.00012
Ammoniacal nitrogen collected in the condensation waters.....		0.00012
Organic nitrogen in condensation waters		0.00220
Sum.....		0.00244

SECOND PERIOD. NO SPRINKLING.

Ammoniacal nitrogen in dilute sulfuric acid.....	0.000007
" " " condensed water..	0.000007
Organic " " " "	0.000040
Sum.....	0.000054

Conclusions.—The exhalation of nitrogenous compounds takes place with a certain relative activity, about two milligrams in two months and a half, as long as the soil is kept moist by sprinkling.

In the second period, without sprinkling, the exhalation is reduced to a mere trace.

The vessel containing the dilute sulfuric acid placed near the porcelain pot absorbs only about one-half of the ammoniacal nitrogen set free. The nitrogen emitted under other forms than ammonia is, in every instance, greatly superior in quantity, and this is the most important of the observed phenomena. This is true at least with the kind of soil with which the experiment was made. With arable soil containing 20 times as much nitrogen as the soil described above this order is reversed,⁴¹ the ammoniacal prevailing over the non-ammoniacal nitrogen volatilized.

These phenomena are doubtless greatly influenced in soil under culture by microbes, and the lowest orders of vegetation to which are doubtless due the traces of non-ammoniacal volatile nitrogenous compounds, a sort of vegetable ptomaines.

454. General Conclusions.—In the light of our present knowledge concerning the methods of nitrogen determination in the soil in the form of organic compounds and ammonia, moist combustion with sulfuric acid is to be preferred to the older methods. For the nitrogen combined as ammonia, the extraction of the sample with hydrochloric acid and subsequent distillation with an excess of freshly calcined magnesia, are recommended. For the study of the progressive decomposition of the nitrogenous compounds, the various processes devised by Berthelot and André are the best.

The origin of the nitric acid in the soil, the methods of studying the various nitrifying organisms, and of estimating the nitric acid produced, will form the subject of part seventh and be further considered in the second volume.

⁴¹ *Annales de Chimie et de Physique*, 1890, [6], 19 : 492.

455. Official Methods for the Analysis of Soils.—Inasmuch as the official methods of soil analysis are used very generally by analysts in the United States they are given below seriatim, although most of them have been discussed under the separate classes of examinations described and compared in the foregoing paragraphs.⁴²

1. Preparation of Sample.—Surface accumulations of decaying leaves, etc., should be removed and a slice of uniform thickness from the surface to the desired depth should be secured. To eliminate the effects of accidental variations in the soil, select specimens from five or six places in the field and remove several pounds of the soil, to the depth of six inches, or to the change between the surface soil and the subsoil, in case such change occurs between the depth of six and 12 inches. In no case is the sample to be secured to a greater depth than 12 inches. If the surface soil extend to a greater depth, a separate sample below the depth of 12 inches is to be obtained. If the surface soil extend to a depth of less than six inches, and the difference between it and the subsoil is unusually great, a separate sample of the surface soil should be secured, besides the one to the depth of six inches.

The depth to which the sample of subsoil should extend will depend on circumstances. It is always necessary to know what constitutes the foundation of a soil, to the depth of three feet at least, since the question of drainage, resistance to drought, etc., will depend essentially upon the nature of the substratum. But in ordinary cases ten or 12 inches of subsoil will be sufficient for the purposes of examination in the laboratory. The specimen should be obtained in other respects precisely like that of the surface soil, while that of the material underlying this subsoil may be sampled with less exactness, perhaps at some ditch or other easily accessible point, and should not be broken up, but left, as nearly as possible, in its original state. Mix these soils intimately, remove any stones, shake out all roots and foreign matters, expose in thin layers in a warm room till thoroughly air-dry, or dry in an air-bath at a temperature of 40°.

The soil is rapidly dried to arrest nitrification. It is not heated

⁴² Bulletin No. 46, Bureau of Chemistry : 71 et seq.

above 40° lest there be dissipation of ammonium compounds, or a change in the solubility of the soil. The normal limit to which the soil may be heated in place by the sun's rays should not be exceeded in preparing a soil for an agricultural chemical analysis.

Five hundred grams or more of the air-dried soil, which may be either the original soil or that which has been passed through a sieve of coarser mesh, are sifted through a sieve with circular openings one-half millimeter in diameter, rubbing, if necessary, with a rubber pestle in a mortar until the fine earth has been separated as completely as possible from the particles that are too coarse to pass the sieve. A three millimeter sieve should be used when the determinations are made on 100 grams or more of soil. The fine earth is thoroughly mixed and preserved in a tightly stoppered bottle, from which the portions for analysis are weighed.

The coarse part is weighed and examined microscopically or with Thoulet's solution.⁴³

It may sometimes be necessary to wash the soil through the one-half millimeter sieve with water; but this is to be avoided whenever possible.

2. *Determination of Moisture*.—Heat from two to five grams of the air-dried soil in a flat-bottom, tared platinum dish for five hours in a water oven kept briskly boiling; cover the dish, cool in a desiccator, and weigh. Repeat the heating, cooling, and weighing at intervals of two hours till nearly constant weight is found, and estimate the moisture by the loss of weight. Weigh rapidly, to avoid absorption of moisture from the air.

3. *Determination of Volatile Matter*.—Heat the dish and dry soil from the above determination to full redness, until all organic matter is burned away. If the soil contain appreciable quantities of carbonates, the contents of the dish, after cooling, are moistened with a few drops of a saturated solution of ammonium carbonate, dried and heated to dull redness to expel salts of ammonium, cooled in the desiccator, and weighed. The loss in weight represents the organic matter, water of combination, salts of ammonium, etc.

4. *Determination of Acid-Soluble Materials*.—In the following scheme for soil analysis it is intended to use the air-dried soil from

⁴³ Principles and Practice of Agricultural Analysis, 1 : 297.

the sample bottle for each separate investigation. The determination of moisture, made once for all on a separate portion of air-dried soil, will afford the datum for calculating the results of analysis upon the soil dried at the temperature of boiling water. It is not desirable to ignite the soil before analysis, or to heat it so as to change its chemical properties.

The acid digestion is to be performed in a flask so arranged that the evaporation of acid shall be reduced to a minimum, but under atmospheric pressure and at the temperature of boiling water. The digestion is easily accomplished in a flat-bottom conical flask of hard glass, carrying a stopper and hard-glass condensing tube at least 18 inches long. Where sulfuric acid is to be determined, a rubber stopper can not be used. A flask with ground-glass stopper, carrying a condensing tube, is useful in such cases.

The flask must be immersed in the water-bath up to the neck, or at least to the level of the acid, and the water must be kept boiling continuously during the digestion.

In the following scheme ten grams of soil are used, this being a convenient quantity of most soils, in which the insoluble matter is about 80 per cent. If desired, a larger quantity of such soil may be used, with a proportionately larger quantity of acid, and making up the soil solution to a proportionately larger volume. In very sandy soils, where the proportion of insoluble matter is 90 per cent or more, 20 grams of soil are to be digested with 100 cubic centimeters of acid and the solution made up to 500 cubic centimeters; or a larger quantity may be used, preserving the same proportions. It is very important that the analyst assure himself of the purity of all the reagents to be used in the analysis of soils before beginning the work.

(a) *Acid Digestion of the Soil*.—Place ten grams of the air-dried soil in an erlenmeyer flask of from 150 to 200 cubic centimeters capacity, add 100 cubic centimeters of pure hydrochloric acid of specific gravity 1.115, insert the stopper with condensing tube, place in a water- or steam-bath, and digest for ten hours continuously at the temperature of boiling water, shaking once each hour. Pour the clear liquid from the flask into a small beaker and wash the residue out

of the flask with distilled water on a filter, adding the washings to the contents of the beaker. The residue, after washing until free of acid, is dried and ignited, as directed below. Oxidize the organic matter present in the filtrate with nitric acid and evaporate to dryness on the water-bath, finishing on a sand or air-bath to complete dryness; take up with hot water and a few cubic centimeters of hydrochloric acid, filter, wash free of chlorids, and again evaporate to complete dryness as before. Take up as before, filter, and wash thoroughly with cold water, or with hot water slightly acidified at first with hydrochloric acid. Cool and make up to 500 cubic centimeters. This is solution A. The residue is to be added to the main residue and the whole ignited and weighed, giving the "insoluble matter." (See 5, Determination of acid insoluble materials, page 516).

(b) *Determination of Ferric Oxid, Alumina and Phosphoric Acid, Collectively.*—To 100 or 200 cubic centimeters of solution A, according to the quantity of substances in solution add ammonium hydroxid to slightly alkaline reaction to precipitate ferric and aluminic hydrates and phosphates. Expel the excess of ammonia by boiling, allow to settle, and decant the clear solution through a filter; add to the flask 50 cubic centimeters of hot distilled water, boil, settle, and decant as before. After pouring off all the clear solution possible, dissolve the residue with a few drops of hydrochloric acid and precipitate again with ammonium hydroxid exactly as before; transfer all the precipitates to the filter and wash with hot distilled water till the washings become free from chlorids. Save the filtrates and washings which form solution B. Dry the filter and precipitate, transfer the precipitate to a tared platinum crucible, burn the filter, and add the ash to the precipitate; ignite to bright redness, cool in a desiccator, and weigh. The increase of weight, minus the ash of filter and the phosphoric acid (found in a separate process), represents the weight of the Fe_2O_3 and Al_2O_3 .

(c) *Determination of Manganese.*—Concentrate the filtrates and washings (solution B) to 100 cubic centimeters or less; add ammonium hydroxid to alkalinity; add bromin water and heat to boiling, keeping the beaker covered with a watch crystal; as the

bromin escapes the beaker is allowed to cool somewhat, more ammonia and bromin water being added and heated as before. This process is continued until the manganese is completely precipitated, which requires from 15 to 30 minutes. The solution is then to be slightly acidified with a few drops of acetic acid and filtered while still boiling hot, the precipitate washed with hot water, dried, ignited, and weighed as Mn_2O_4 .

(d) *Determination of Calcium*.—If no manganese be precipitated, evaporate solution B or the filtrates and washings from (c) to about 50 cubic centimeters, make slightly alkalinity with ammonia, and add, while still hot, ammonium oxalate solution so long as any precipitate is produced, adding a few cubic centimeters in excess to convert the magnesium also into oxalate. Heat to boiling, allow from 15 to 20 cubic centimeters of hot distilled water on the precipitate, and again decant the clear solution on the filter. Dissolve the precipitate in the beaker with a few drops of hydrochloric acid, add a little water, and reprecipitate, boiling hot, by adding ammonium hydroxid to slight alkalinity and a little ammonium oxalate solution; filter through the same filter, transfer the precipitate to the filter, and wash it free from chlorids; dry, ignite the precipitate over the blast lamp until it ceases to lose weight, weigh, and estimate as CaO .

(e) *Determination of Magnesium*.—Slightly acidify the filtrate and washings from (d) with hydrochloric acid and concentrate to about 50 cubic centimeters, place in a small erlenmeyer flask or beaker, make slightly alkaline with ammonium hydroxid, and add sufficient acid sodium phosphate solution to precipitate the magnesium; then add gradually ten cubic centimeters of strong ammonium hydroxid, cover closely to prevent escape of ammonium, and let stand in the cold. Filter after 12 hours, wash the precipitate free from chlorids, dry, burn at first at a moderate heat, finally igniting intensely, and weigh as $Mg_2P_2O_7$.

(f) *Determination of Ferric Oxid*.—Evaporate 100 cc. of solution A, with the addition of about ten cubic centimeters of sulfuric acid, until all hydrochloric acid is expelled; dilute with water, reduce with zinc, and estimate iron oxid by a stand-

ard solution of potassium permanganate. To prepare potassium permanganate solution, dissolve 3.156 grams of the pure salt in 2,000 cubic centimeters of distilled water, and preserve in a glass-stoppered bottle, shielded from the light. Standardize this solution after it has stood 24 hours with pure ammonia-ferrous sulfate, oxalic acid, or freshly dissolved metallic iron.

Instead of using another portion of the solution, the weighed precipitate from (b) may be dissolved by digestion on the water-bath in a covered beaker or flask with from ten to 20 cubic centimeters of a mixture of one part H_2SO_4 , with four parts of water.

Deduct the per cent of ferric oxid obtained from the per cent of ferric oxid and alumina (b), and make corrections for filter ash and phosphoric acid, to obtain the per cent of alumina.

(g) *Determination of Phosphoric Acid*.—Evaporate from 100 to 200 cubic centimeters of solution A to about 25 or 30 cubic centimeters; nearly neutralize with ammonium hydroxid, add about ten grams pure crystallized ammonium nitrate, and gradually about 20 cubic centimeters molybdic solution ((1) (b), p. 11) and set in water-bath at a temperature of 40° . When the precipitate has settled sufficiently, draw out with a pipette about five cubic centimeters of the clear liquid, and test it by allowing it to run into five cubic centimeters of warm molybdic solution. If any precipitate be produced, the test liquid is returned to the main portion and more molybdic solution is added and the operation repeated until all the phosphoric acid is precipitated. After standing from eight to 12 hours at a temperature not above 40° , the ammonium phosphomolybdate mixture is filtered and the phosphoric acid determined as magnesium pyrophosphate. It is recommended to redissolve the magnesium ammonium phosphate precipitate in acetic acid, after it has been washed once or twice, and reprecipitate with ammonia and a fresh quantity of magnesia mixture, giving the usual time for the separation of the precipitate. If there be any residue of phosphates remaining on dissolving the phosphomolybdate in ammonia, or the magnesium ammonium phosphate in acetic acid, this residue is dissolved in a little hydrochloric acid, neutralized with ammonium hydroxid and precipitated with molybdic solu-

tion, and the phosphomolybdate obtained added to the main quantity.

(b) *Optional Provisional Method.*—Proceed as in (a) “until all the phosphoric acid is precipitated,” and then finish the determination as follows:

After standing for three hours at a temperature not above 50°, filter on a small filter, wash with water until two fillings of the filter do not greatly diminish the color produced with phenolphthalein by one drop of standard alkali. Place the filter and precipitate in the beaker and dissolve in standard alkali, add a few drops of phenolphthalein solution and titrate with standard acid, one cubic centimeter of which equals 0.0005 gram of phosphoric acid (P_2O_5).

(h) *Provisional Method for Determining Phosphoric Acid.*—Ten grams of the air-dried soil, passed through a sieve of one millimeter mesh, are placed in a small kjeldahl flask marked at 250 cubic centimeters. From 20 to 30 cubic centimeters concentrated sulfuric acid and approximately 0.7 gram yellow oxid of mercury are added, the contents of the flask well mixed by shaking, and oxidizing over the open flame, as in the determination of nitrogen, for an hour. After cooling, about 100 cubic centimeters of water, five cubic centimeters of concentrated hydrochloric and two cubic centimeters nitric acid are added, and the mixture reboiled to oxidize the iron, cooled, the volume completed to the mark with water, and the contents of the flask filtered through a dry, folded filter paper. One hundred cubic centimeters of the filtrate are placed in a flask of about 450 cubic centimeters capacity, strong ammonia added until a permanent precipitate is formed, which is dissolved by the addition of about seven cubic centimeters of nitric acid, and the mixture boiled until clear. The flask is removed from the flame and cooled at room temperature for exactly two minutes, 75 cubic centimeters molybdate solution added, and the flask placed in a water-bath kept at 80° for 15 minutes, shaking vigorously four or five times meanwhile. After removing from the bath, the flask is allowed to stand for ten minutes until the precipitate has settled, and the supernatant liquid is poured onto the filter paper under pressure, the

precipitate being partially brought upon the paper. The flask and precipitate are thoroughly washed with ammonium-nitrate solution, and the precipitate separated either by decantation or on the filter paper. The flask is placed under the funnel, the precipitate is dissolved in ammonia, and the phosphoric acid estimated by usual processes.⁴⁴

(i) *Determination of Sulfuric Acid.*—Evaporate 100 or 200 cubic centimeters of solution A nearly to dryness on a water-bath to expel the excess of acid; add 50 cubic centimeters of distilled water; heat to boiling and add from two to three cubic centimeters of a solution of barium chlorid, and continue the boiling for five minutes. When the precipitate is settled, pour the liquid on a tared gooch, treat the precipitate with from 15 to 20 cubic centimeters of boiling water, and transfer to the filter and wash with boiling water, at first slightly acidified with a few drops of hydrochloric acid, and finally with pure water, till the filtrate is free from chlorids. Dry the filter, ignite, and weigh as barium sulfate, which multiplied by 0.34331 equals SO_3 .

(j) *Determination of Potash and Soda.*—Treat the filtrate from (j) with ammonium hydroxid exactly as in (b). Evaporate the filtrate and washings to dryness, heat below redness, until ammonium salts are expelled, dissolve in about 25 cubic centimeters of hot water, add five cubic centimeters of baryta water, and heat to boiling; let settle a few minutes, and test a little of the clear liquid with more baryta water to be sure that enough has been added. When no further precipitate is produced, filter and wash thoroughly with hot water. Add ammonia and ammonium carbonate to complete the precipitation of the barium, let stand a short time on the water-bath, filter and wash to precipitate thoroughly with hot water, evaporate filtrate and washings to dryness in a porcelain dish, expel ammonium salts by heat below redness, take up with a little hot water, add a few drops of ammonium hydroxid and a drop or two of ammonium carbonate, let stand a few minutes on the water-bath, filter into a tared platinum dish, evaporate to dryness on the water-bath and heat to dull redness, until all ammonium salts are expelled and the residue is nearly or

⁴⁴ Bulletin No. 43, Division of Chemistry : 58-60.

quite white. The heat must not be sufficient to fuse the residue. The weight of the residue represents potassium and sodium chlorids. Determine the potassium present with platinum chlorid in the usual manner. The sodium chlorid is obtained by subtracting potassium chlorid thus found from the total weight of the two chlorids.

Instead of the filtrate form (j), a fresh aliquot portion of solution A may be evaporated to dryness, redissolved in water and treated directly with milk of lime as in ash analysis; but without previous addition of barium chlorid.

5. *Determination of Acid-Insoluble Materials.*—The residue from 4 (a) may be analyzed by the usual methods for silicates. If it be desired to determine the silica soluble in alkalies, the residue must be dried at 100° and an aliquot portion removed before ignition for treatment with sodium carbonate solution. Another aliquot portion, or the rest of the residue, is ignited and weighed.

6. *Determination of Total Alkalies.*—Determine in a separate portion of the soil by J. Lawrence Smith's method⁴⁵; or, preferably, determine by this method the alkalies in the insoluble residue from 4 (a) and add the amount obtained from the hydrochloric acid solution.

7. *Identification of Lithium, Caesium, and Rubidium.*—The salts of these elements are occasionally found in very small amounts in soils. Their agricultural uses are still in question, and their amount is too small to admit of quantitative estimation. A qualitative examination may be made by the spectroscope with the water-soluble materials evaporated to dryness and dissolved with two or three drops of hydrochloric acid or with the alkaline chlorids separated as in 4 (k) or 6.

8. *Determination of Total Nitrogen in Presence of Not More Than a Trace of Nitrates.*—From seven to 14 grams of the soil are placed in a small kjeldahl digesting flask of about 250 cubic centimeters capacity with 30 cubic centimeters of strong sulfuric acid, or more, if necessary, and 0.7 gram of yellow oxid of mercury and boiled for an hour. The residue is oxidized with potassium permanganate in the usual way. After cooling the

⁴⁵ Crookes's Select Methods, 2nd edition : 28-40.

flask is half filled with water, vigorously shaken, the heavy matters allowed to subside and the supernatant liquid poured into a flask of from 1,000 to 2,000 cubic centimeters capacity. This process is repeated until the ammonium sulfate is practically all removed and the digestion flask is a little more than half full and the ammonia then distilled in the usual manner. Where more than a trace of nitrates is present the methods of procedure, described in volume second of this manual, are to be followed.

9. *Determination of Carbon Dioxid.*—In from five to ten grams of the sample in any of the usual forms of apparatus determine the carbon dioxid evolved on treatment with an acid by increase of weight in the potash absorption bulbs.

10. *Determination of Humus.*—Ten grams of the sample are placed in a gooch, extracted with one per cent hydrochloric acid until the filtrate gives no reaction with ammonia and ammonium oxalate, and the acid removed by washing with water. The contents of the crucible (including the asbestos filter) are then washed until the filtrate gives no reaction with ammonia and ammonium oxalate, and the acid removed by washing with water. The contents of the crucible (including the asbestos filter) are then washed into a glass-stoppered cylinder with 500 cubic centimeters of four per cent ammonia and allowed to remain, with occasional shaking, for 24 hours. During this time the cylinder is inclined as much as possible without bringing the contents in contact with the stopper, thus allowing the soil to settle on the side of the cylinder, and exposing a very large surface to the action of the ammonia. The cylinder is then placed in a vertical position and left for 12 hours, to allow the sediment to settle to the bottom. The supernatant liquid is filtered and the filtrate must be perfectly clear and free from turbidity; evaporate an aliquot portion, dry at 100° and weigh. The residue is then ignited and again weighed. The humus is calculated from the difference in weights between the dried and the ignited residues.

11. *Determination of Humus Nitrogen.*—Digest the soil with two per cent hydrochloric acid and wash as nearly free of acid as possible with distilled water. Extract the humus with a three per

cent solution of sodium hydrate and determine nitrogen in the extract in the usual way.

12. *Statement of Results.*—All results of soil analysis are to be calculated as per cent of the soil dried to constant weight in the water oven, and are to be stated in the following order:

Insoluble matter.....
Soluble silica.....
Potash (K_2O).....
Soda (Na_2O).....
Lime (CaO).....
Magnesia (MgO).....
Manganese oxid (MnO).....
Ferric oxid (Fe_2O_3).....
Alumina (Al_2O_3).....
Phosphorus pentoxid (P_2O_5).....
Sulphur trioxid (SO_3).....
Carbon dioxid (CO_2).....
Water and organic matter.....

Total.....

Humus.....
Ash.....
 Phosphorus pentoxid.....
 Silica.....
Nitrogen (organic).....
Hygroscopic moisture.....
Moisture absorbed at t°

PART SEVENTH

METHODS OF STUDYING THE ACTIVITY OF NITRIFYING ORGANISMS IN THE SOIL.

456. Introductory Considerations.—The detailed methods for estimating nitrogen in the forms of nitric and nitrous acids belong properly to the second volume of the work which is devoted to a study of fertilizers and manures. Since the existence of these forms of nitrogen in the soil is transient and their production practically continuous they naturally fall into the class of fertilizers rather than of permanent soil constituents. The organisms to which these bodies owe their chief origin in the soil are, however, so general that a study of that part of their activity which results in the formation of nitrates, nitrites and ammonia belongs properly here. It is scarcely necessary to state that this part of the work is in no sense a treatise on soil bacteria. Reference will be made here only to those features of the subject which are necessary to the comprehension of functions of the soil, from a chemical point of view, in producing fertility. For detailed studies of bacterial life and descriptions of methods of culture and isolation, reference is made to the standard works on bacteriology.

457. Organic Nitrogen in the Soil.—With the exception of the small quantities of nitric acid added to the soil directly in rain and snow, the whole supply of this substance, so necessary to plant life, is derived from the oxidation of the nitrogen of the atmosphere or of the organic nitrogen supplied to the soil by decaying animal and vegetable matters.

These products are either stored as the results of past nitrification or are formed synchronously with their consumption by the growing plant. Nitrogenous compounds are present in the soil as organic vegetable or animal remains and as humus. All vegetable and animal material deposited in or on the soil contains more or less of these proteid or nitrogenous matters while the amount of

nitric acid supplied in this way is probably represented entirely by the quantity in the organism of the plant or animal and unabsorbed at the time of its death. In other words it is not demonstrated that nitrates or nitrites are in any sense a special product of plant growth save in the case of nitrifying organisms themselves which are supposed to be of a vegetable nature. Animal organisms do not in any sense assimilate nitric nitrogen.

With most plants, the quantity of proteid nitrogen which they can deliver to the soil is in no case greater than the sum of organic and nitric nitrogen supplied in their food and they can therefore be regarded only as the carriers and conservers of this substance. On the other hand there are some plants, notably those belonging to the leguminous family, which permit of the development on their rootlets of colonies of bacteria which have the faculty of rendering atmospheric nitrogen available for plant growth. Whether or not there exist bodies other than the micro-organisms mentioned which are capable of directly oxidizing and fixing atmospheric nitrogen is still an unanswered question. It is not probable, however, that the difficult task of oxidizing atmospheric or free nitrogen would be accomplished in nature in only one way. In fact it has already been established that organisms do exist which are capable of oxidizing free nitrogen in a manner wholly independent of other plant life and to produce weighable quantities of nitric acid when developed in media of mineral matters and pure carbohydrates to which free nitrogen has access. It is, therefore, fair to assume that the fixation of free nitrogen is a function of chemical activity quite independent of ordinary plant life and that the leguminous plants take no further part in this process than that of providing in their radical development a favorable nidus for the growth of the nitrifying organisms.

By the action of denitrifying organisms a portion of the nitrogen of nitric acid is constantly restored to a free state, a far larger portion, perhaps, than is fixed in the atmosphere itself by the action of electricity. Were it not, therefore, for the activity of the nitrifying ferments the stores of nitrogen available for growing plants would constantly become less. Instead of this being the case, however, it is probable that the contrary is true and that,

by a wise system of agriculture, the total nitrogen at the disposal of plants may become greater and greater in quantity.

It will prove of interest here to refer to the first publication of the Department of Agriculture in so far as it has come to the attention of the author making reference to the nitrifying organisms.⁴⁶

"The sources of nitrogen in crops are the nitrates and ammonia salts, which are seldom present in large quantities and should be used on or generated in the soil as rapidly as crops require them. The process of nitrification whereby inert or unassimilable nitrogen becomes converted into nitric acid is thus of great importance to agriculturists. This (action) is due to a minute *bacterium* present in all soils whereby the humus and ammonia are oxidized and the nitrogen (thereof) converted into nitric acid. This process does not take place unless the soil is moist and has free access of air and some base, generally lime, is present with which the nitric acid can combine. Nitrification is thus most active in summer and ceases apparently in winter."

458. Development of Nitric and Nitrous Acids in Soils.—Owing to the solubility of nitrates there can be but little accumulation of them in soils in those countries where there is any considerable amount of rain-fall. On the other hand in arid regions there may be found extensive deposits of nitrates. The occurrence of a certain quantity of nitrates in the soil, however, is essential to the growth of plants. Until within a few years little was known of the origin of nitric acid in the soil. The presence of nitrates in drainage waters was well established, likewise the consumption of nitric acid by the growing plant, but the method of its supply was unknown. In a general way it was said that the nitric acid came from electrical action and the oxidation of the albuminous bodies in the soil, but without specifying the manner in which this change takes place. The researches of Hellriegel, Schlösing and Müntz, of Springer, Winogradsky, Frankland, Warington and others have demonstrated the fact that this oxidation is caused by bacteria and that the nitrates formed can be consumed and destroyed

⁴⁶ Department of Agriculture, Annual Report, 1885; 165.

by other species of this organism. In the one case the process has been called nitrification and in the other denitrification.⁴⁷

The influence of these low organisms both in producing fertility in a soil and maintaining it in a state of fertility is of the highest importance.

459. Conditions Necessary for Nitrification.—In order to properly understand the reasons for many of the steps in investigating a soil for nitrifying organisms, it will be useful to state the general conditions on which nitrification depends.

The nitrifying organism, like every other one, first of all feels the necessity for food. In general, food which is given to microbes of all kinds consists of some organic matter together with the addition of mineral substances necessary to growth. These substances in general are phosphoric acid, potash, and lime. Of these articles of bacterial food phosphoric acid seems to be the most important. With the nitrifying organisms, however, it has been found that the organic matter can be omitted. In fact, as will be seen further on, the omission of organic matter supplies the best condition for the proper isolation of the organisms. In other words some forms of the nitrifying organisms have the property of subsisting wholly on mineral substances, *i. e.*, are true vegetables.

The presence of oxygen is also necessary to the growth of the common nitro-organisms. In an atmosphere deprived of oxygen or in which the oxygen is reduced to a very low percentage, the process of nitrification is retarded or stopped as the oxygen diminishes or disappears.

There are, however, some groups of nitrifying organisms which are able to assimilate considerable quantities of nitrogen in the absence of free oxygen. These are known as anaerobic ferments.

The presence of a base with which the nitrous or nitric acid formed may unite is also essential to the proper conduct of the process. For this reason the nitrification should take place in a

⁴⁷ *Comptes rendus*, 1877, **84** : 301 ; 1879, **89** : 891 ; *Journal of the Chemical Society (Trans.)*, 1878, **83** : 44 ; 1879, **85** : 429 ; 1884, **45** : 637 ; *American Chemical Journal*, 1882-83, **4** : 452 ; *Proceedings of the American Association for the Advancement of Science*, 1892, **41** : 93 ; *Annales de l'Institut Pasteur*, 1890, **4** : 213, 257, 760 and **5** : 92.

solution which is feebly alkaline or in the presence of a base which can be easily decomposed so that no acidity can be established. Calcium carbonate is a base well suited to favor the nitrifying process and its presence in a soil favors the rapid oxidation of proteid matter. The mistake must not be made, however, of supposing that an excess of alkali would favor nitrification. The contrary is true. A slight excess of alkali may prevent nitrification altogether when it is due to the common organisms present in an arable soil. It may be that in soils charged with alkali a different organism exists which is capable of exercising its functions when the alkali is in excess.

The temperature to which the nitrifying body is subjected is also a matter of importance. The nitrifying organisms have the property of remaining active at lower temperatures than most bodies of their class. On the contrary, their action is retarded and destroyed by high temperatures. The most favorable temperature for nitrification is about that of blood heat; *viz.*, 37°. At 50° the organism shows very little activity and at 55° its activity ceases altogether. Nitrification, however, according to Warington, cannot be started in a solution if the initial temperature is 40°.

Desiccation has the same retarding influence on nitrification that a high temperature has. Even thoroughly air-drying a soil may paralyze its nitrifying qualities.

Darkness is also necessary to the proper progress of nitrification. In a strong light, the activity of the organism is very much diminished or destroyed altogether. A bright light like sunshine may even stop nitrification which has set in.

460. Determination of Nitrifying Power of Soils.—In studying the distribution of the nitrifying organisms in a soil the general method of procedure is based on the production of nitrification in a convenient solution by the organisms present in a given sample of soil. If the solution seeded with the given portion of soil remain unaffected, it will show that there were no nitrifying organisms present in the seed used. On the other hand, the vigor of the nitrifying process when once it is started, may be taken as an evidence of the number and activity of the organisms in the soil, a sample of which was used for seed.⁴⁸

⁴⁸ See paragraph 467.

461. Effect of Potassium Salts on Rate of Nitrification.—Dumont and Crochetelle have described some experiments to determine the effect of potassium salts alone and in combustion with lime on nitrification.⁴⁹

A soil rich in vegetable mold (18.5 per cent of humus and 0.29 per cent of lime) was treated with varying amounts of potassium sulfate and carbonate and kept for 20 days at 25°. In the untreated soil the amount of nitric acid produced was 25 parts per million. When potassium carbonate was applied in quantities of from one-tenth to six per cent the amount of nitric acid increased from 47 parts per million to 438 parts when four and one-half per cent of the potassium salt were used. Larger quantities caused a decrease in the amount of nitric acid produced. Very little effect, on the contrary, was produced by the action of potassium sulfate. When one-half per cent was employed the quantity of nitric acid formed rose to 50 parts per million, while with quantities as high as five per cent it fell below the normal; *viz.*, 25 parts per million.

When calcium carbonate was added to the soil in conjunction with potassium sulfate there was a marked increase in the amount of nitrogen oxidized. The activity of potassium sulfate in promoting nitrification is therefore increased by the presence of the calcium salt, potassium carbonate and calcium sulfate being formed.

These results show that the nitrification was promoted by alkaline salts or neutral carbonates, while a neutral sulfate was practically ineffective.

462. Production of Nitrous and Nitric Acids.—In the following pages the study of the methods of isolating the nitrous and nitric ferments will be considered as one process, the final isolation of the two classes of bodies being the result of their synchronous cultivation in appropriate media. The special process of the production of ammonia by oxidation is not so well-known, and will therefore be described in brief.

It is now generally conceded, as shown by the comparative ex-

⁴⁹ Comptes rendus, 1894, 118 : 604.

periments conducted in the Bureau of Chemistry, given in paragraphs 467 and following, that the action of the nitrous organism is precedent to that of the nitric, but the two processes go on so nearly together as to prevent the accumulation of any large quantities of the lower salt in the soil.

Whether or not the formation of ammonia precedes that of nitrous acid is still a subject for experimental demonstration. Chemically, both nitrous acid and ammonia may be produced by the reduction of nitric acid, but the ammonia thus formed may pass through the nitrous acid state. In nature, the reverse of this process may be the customary method.

463. Production of Ammonia in the Soil by the Action of Microbes.—It is highly probable as intimated above, that organic nitrogen in the soil in passing into the form of nitric acid exists at some period of the process in the form of ammonia.

Marchal has isolated and studied some of these ammonia-making bacteria.⁵⁰ *Bacillus mycoides* is the most active of these organisms. It occurs constantly in surface soils and is present in the air and in natural waters. In decomposing albumen it produces a strongly alkaline solution due to ammonium carbonate. Organic carbon, during this process, is converted chiefly into carbon dioxid, but small quantities of formic, propionic, and butyric acids are also produced. Any organic sulfur which is present is converted into acid. No hydrogen or nitrogen is eliminated in a free state. While slight alkalinity is favorable to the development of this bacterium, yet it may be propagated in a feeble sulfuric acid solution when the acid is less than one per cent.

The greatest activity of this organism is manifested at 30°. Below 5° and above 42° no ammonia is produced. The bacillus will not develop in an atmosphere of hydrogen or carbon dioxid, except in solutions of organic matter and nitrate. In addition to its action on egg albumen it decomposes other proteid bodies as well as leucin, tyrosin, creatin, and asparagin. It, however, does not oxidize urea, nor does it develop in solutions of ammonium salts and nitrates, except as mentioned above. When soluble carbo-

⁵⁰ Bulletin de l'Académie royale de Belgique, 1894, [3], 25 : 727; Journal of the Chemical Society, London, 1894, 66, part 2 : 248.

hydrates are present, acids are formed. It is concluded from these experiments that the final oxidation of organic nitrogenous matter is preceded by its conversion into ammonium carbonate.

464. Summary of Statements.—All nitrogenous matters which would be naturally present in the soil may become subject to nitrification when the proper conditions are supplied. Munro has also succeeded in nitrifying ethylamin, thiocyanates, and gelatin, urea, asparagin, and the albuminoids of milk and rape-seed.

The chief products of nitrification are ammonia, nitrous or nitric acid, carbon dioxid, and water. The ammonia and nitrous acid may not appear in soils as the final products of nitrification, as the nitric organism attacks the latter at once and converts it into nitric acid. Nitrous acid and ammonia may also be produced in soils as one of the retrograde steps in denitrification.

To summarize the conditions necessary for proper nitrification it may be said that first, the proper material must be supplied; *viz.*, an organic or inorganic nitrogenous compound capable of oxidation. In the second place, the medium must be faintly alkaline, the temperature must not be too high, nor too low, the nitrifying organisms must have abundant food, and the process must take place in the dark.

465. Order of Oxidation.—It is quite definitely determined that activity of the ammoniacal and nitrous organisms is the first step in the process, since the nitric organism appears to have no power whatever to oxidize proteid compounds; while, on the other hand, the nitrous organism can not, in any case, complete the conversion of nitrous into nitric acid.

The conditions which permit certain organisms to oxidize free nitrogen have not been definitely determined. The presence of such bodies in the tubercles attached to the rootlets of certain leguminous plants has been established. These organisms are not able to exert their activity in the soil alone and will be described in the second volume of this work. Lately, Winogradsky has isolated from the soil a nitrifying organism which is capable of converting free nitrogen into forms suited to nourish plant growth. This organism is cultivated in dextrose with careful exclusion of all nitrogen, save that which exists in the air carefully freed of every trace of ammonia or oxidized nitrogen.

Under the influence of the growth of this organism the sugar undergoes a butyric fermentation, and nitrogen in an oxidized form is assimilated in an amount apparently equal to about one five-hundredth of the sugar consumed.

This result leads Warington⁵¹ to remark that it is a fact of extraordinary interest, both to the physiologist and chemist, that a vegetable organism should be able to acquire from the air all the nitrogen it needs.

466. The Nitrification of Ammonia.—The same organism which converts organic nitrogen into nitrous acid acts also on ammonia and its compounds with a similar result. In fact, the formation of ammonia may be regarded as one of the stages on the road from albuminoid to nitric nitrogen.

Data have been collected by Schlösing on the nitrification of ammonia taking place in arable soil, tending to show that this phenomenon is accomplished without appreciable loss of nitrogen in the gaseous state.⁵² This, however, does not hold good when the quantity of ammonium carbonate introduced into the earth is largely increased. In two experiments, conducted by Schlösing, with a larger quantity of ammonium carbonate, the loss of nitrogen was very notable. In certain conditions the production of nitrous acid may take place, and it is interesting to know whether the appearance of nitrites has any influence on the disengagement of free nitrogen. In order to determine this question a solution of calcium nitrite was prepared by decomposing silver nitrite with calcium chlorid. From the results of the experiments made it was seen that the nitrites were only the results of a retarded and partially incomplete nitrification. They, are, moreover, thus an obstacle to the normal work of the nitrifying organisms. It is also established that when they are present a disengagement of gaseous nitrogen takes place, whether the nitrites are formed during the progress of the experiment, or whether they were originally present. However, it is not best to say that the nitrites themselves have been the cause of the disengagement of the nitrogen. It may happen that the disengagement of the nitrogen and

⁵¹ Chemical News, 1893, 68 : 175.

⁵² Comptes rendus, 1889, 109 : 883.

the presence of nitrites are simply simultaneous and due to one and the same cause. The destruction of nitrates in the midst of reducing agents furnishes, according to the nature of these bodies and the circumstances, nitrous acid, nitrogen dioxid, nitrogen protoxid, free nitrogen, and even ammonia.

This destruction of nitrates and the appearance of oxids of nitrogen and of free nitrogen are more likely to be due to the presence of a separate denitrifying ferment as pointed out by Springer than to have arisen in the manner mentioned above by Schlössing. In the present state of our knowledge, moreover, we can hardly regard the presence of nitrites as an obstacle to complete nitrification. On the other hand, it seems to be well established that the production of nitrites or ammonia is a necessary step between organic nitrogen and nitric acid.

467. Activity of the Nitrifying Organisms in Soils.—To determine the activity of the nitrifying organisms in soils—that is, those of the nitrous and nitric classes—the author in conjunction with Ewell, in 1895, devised the plan which is described below. The object of the investigation was to determine the activity of the ferments in the soil without attempting in any way to count or isolate them. In other words, it is purely an analytical process to ascertain a certain property of the sample under examination. By collecting samples at the same time and under the same conditions from widely separated localities the comparative nitrifying properties of soils may be determined.

468. Sampling Tubes.—The tubes described in 75 are conveniently used for the present purpose. The rubber caps over the ends should be of different colors to distinguish before removing the cutting from the blunt end. The blunt end is closed with a plug of cotton and a similar plug is placed in the bottom of the cap of the cutting end in such a way that it is not disturbed when the cap is removed at the time of sampling. This plug takes the place of the rubber ball used to prevent the cutting of the rubber cap by the sharp edge of the tube.

The caps are put in place and the whole apparatus sterilized by heating for a proper time to the temperature of boiling water. The tubes are then ready without further manipulation for use as above described.

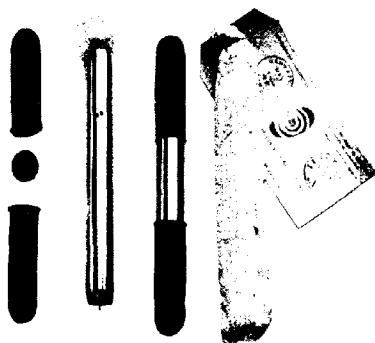


Fig. 83. Sampling Tubes for Determination of Nitrifying Power.

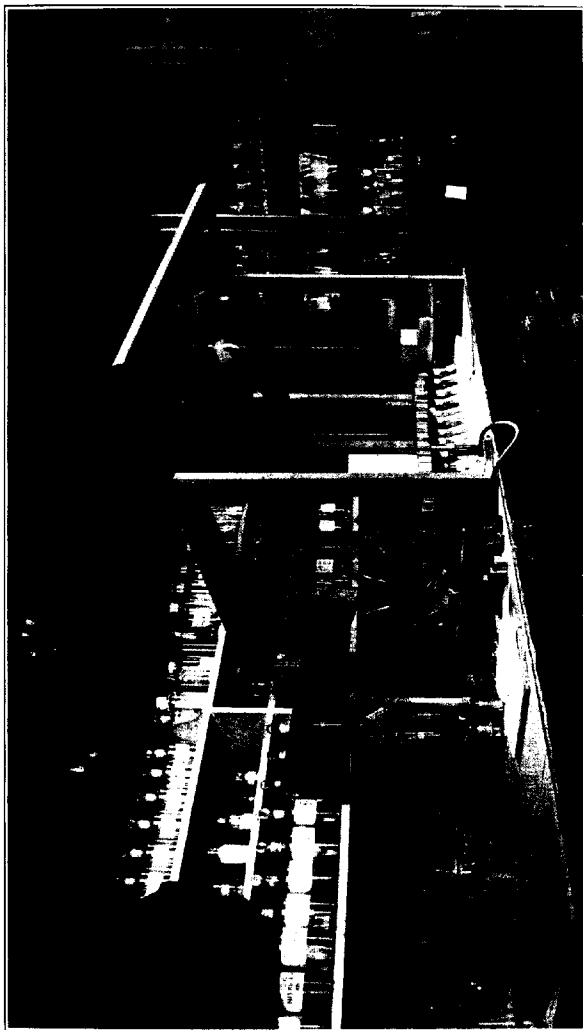


Fig. 84. Glass Hood for Seeding Nitrifying Cultures.

The appearance of the tubes, as prepared for sending the sample by mail, are shown in Fig. 83.

The quantity of soil transmitted in the tubes described above is much greater than is needed for seeding the cultures, but it is necessary to get that amount in order to obtain a representative sample. Each sample is thoroughly mixed before removing the portions for the inoculations. For this purpose a number of small erlenmeyer flasks are plugged with cotton and sterilized in a hot-air sterilizer. Each tube is then carefully opened and its contents pushed into one of the sterile flasks with the aid of a large sterilized glass rod of a diameter slightly less than the internal diameter of the tube. These manipulations are conducted under a glass hood, Fig. 84, with the customary precautions for the transfer of materials from one piece of apparatus to another without contamination with atmospheric organisms.

Before the flasks are again closed, the lumps of soil are broken up and thoroughly mixed with the fine soil by means of a sterilized glass rod or a sterilized platinum spatula.

469. Collecting Samples.—By following carefully the directions given below, it will be possible to secure small samples of soil free from other micro-organisms than those normally contained therein:

The tubes and their rubber caps are carefully sterilized and should not be removed from their cloth envelopes until the moment of sampling. After the sample has been secured and the cap replaced on the tube, the latter should be immediately enclosed in the cloth sack and labeled with one of the tags therewith enclosed. The samples should represent at least two kinds of soil, in one instance the cultivated soil, which is most characteristic of plots, and in the second place a virgin soil of the same type. The virgin soil may be either soil which has been covered with grass or in forest. The spots at which the sampling is to be done are selected, and the tags for each tube are prepared beforehand so as to avoid delay at the time of sampling. A pit with straight walls is dug, the sides of which are at least two feet wide and even three feet would be better. The pit is at least 42 inches deep. One of the sides having been made perfectly smooth, and without

allowing the loose fragments from the top to fall down and adhere to the walls below, the spots at which the samples are to be secured are marked with a tape line at the following points; *viz.*, 3, 15, 27, and 30 inches, respectively, below the surface. Beginning at the bottom point, scrape off the surface of the wall over an area slightly larger than that of the end of the sample tube by means of a spatula, which, just previous to use, has been held for a moment or two in the flame of an alcohol or other convenient lamp. The sample tube having been removed from its sack, it will be noted that the end covered with black rubber is the one which is to be held in the hand, and this black rubber cap should be first removed, being careful not to extract the plug of sterilized cotton which closes the end of the tube. Holding the tube firmly by the end, the fingers extending only about two inches from the end, remove the light colored cap and push the tube with a turning motion into the side of the pit at the point where the surface has been removed with the sterilized spatula. When this is properly done the tube will be filled with a cylinder of soil equal to the length of the part of the tube penetrating the wall of the soil. The tube is withdrawn, the light rubber cap first replaced, and then the black one. The light rubber cap is held in the hand during the process with the mouth down so that no dust or particles of soil are permitted to contaminate its inner walls. For the same reason after the removal of the light rubber cap the brass tube should be carefully preserved from dust or fragments, the open end, that is the cutting end, being held downward until ready for use. After one tube has been filled, capped, replaced in the sack and labeled, the spatula should be again sterilized and samples taken in regular order until the top one is finished. The tubes are sent by mail.

470. The Culture Medium and Seeding.—The solution of ammonium sulfate and nutritive salts used as the culture medium for this series of investigations has the following composition:

	Grams.
Ammonium sulfate	0.942
Potassium phosphate	1.000
Magnesium sulfate	0.0
Calcium chlorid.....	trace
Distilled water	1000 cc.

These are the so-called "chemically pure" reagents usually at hand in the laboratory. The solution does not contain more than the merest traces of organic matter.

One hundred cubic centimeters of this solution are placed in each of several sterilized Erlenmeyer flasks of, from 150 to 200 cubic centimeters capacity. The cotton plugs are returned to the flasks, glass caps are placed over them, and the flasks thus charged are sterilized in a steam sterilizer in the usual manner, being heated for the proper length of time on each of three successive days. Some freshly precipitated and carefully washed calcium carbonate is also prepared and sterilized in similar flasks, after mixing with such a quantity of water that five cubic centimeters of the well-shaken mixture contains in suspension a little more than 0.2 gram of calcium carbonate.

It is believed to be impracticable to weigh the portions of soil used for seeding the cultures without contaminating them with organisms contained in the air and adherent to floating dust. Moreover, since the moisture content of the samples varies considerably, it is thought that a measured quantity is more satisfactory than one weighed. Portions of each sample are therefore transferred to each of three culture flasks by means of a sterilized platinum spoon holding between 0.4 and 0.5 gram of a moderately moist soil. To each of two of the three flasks seeded with a given sample, there is added by means of a sterilized pipette approximately 0.2 gram of the sterilized calcium carbonate referred to above. No calcium carbonate or other agent for the neutralization of the nitrous and nitric acids formed, and the sulfuric acid set free as the nitrification progressed, is added to the third flask seeded with each sample of surface soil. From this series of cultures containing no neutralizing agent the data in regard to the influence of acidity upon the activity of the nitrifying organisms referred to were obtained⁵⁵.

In the case of each sample from a greater depth than three inches only two cultures are prepared and to both of these calcium carbonate is added.

⁵⁵ Journal of the American Chemical Society, 1896, 18 : 475.

471. Temperature Considerations.—When a thermostat of sufficient dimensions to hold all the cultures is not available, the culture flasks are placed in a dark closet, the temperature of which varies with that of the laboratory air. The fluctuations are unfortunately very considerable, and their effect on the rate of nitrification is very marked, as will readily be seen on examination of the data presented below. The readings of a maximum and minimum thermometer, kept in the culture closet, are recorded each day. Series of cultures were seeded, as above described, on May 3, 9, 18, 27, June 5, 19, 26, July 13, 19, September 10, October 12, and November 15, 1895. Temperature charts are made to record the maximum and minimum daily temperature throughout the period of eight weeks following each of the dates of seeding.

472. Progress of Nitrification.—At the end of each week following the seeding of the cultures, each culture is tested for the purpose of ascertaining the amount of nitrification accomplished during the preceding seven days. Diphenylamin and concentrated sulfuric acid are the reagents used for this test. At the end of each succeeding week throughout the observation period of eight weeks the amounts of nitrous and nitric acids are determined. For these tests the appropriate portion, and no more, of the culture fluid is removed from each culture flask and transferred to the tube or evaporating dish in which the test is made. A separate sterilized pipette is used for the removal of the liquid from each flask.

473. Methods of Testing for Nitrous and Nitric Nitrogen.—Diphenylamin and concentrated sulfuric acid are used for the purpose of ascertaining the time at which nitrification begins because they react with both nitrous and nitric acids. The depth of the blue color produced by the action of the nitrates or nitrites upon diphenylamin in the presence of concentrated sulfuric acid varies considerably with the temperature and strength of the acid. For the purpose of obtaining comparable results it is necessary that a uniform method of manipulation should be used, and after a number of experiments the following process was adopted:

To one cubic centimeter of the culture solution to be tested which is transferred from a culture flask to a dry test tube by means of a sterilized pipette, there is added one drop of a

solution of diphenylamin in four cubic centimeters of concentrated sulfuric acid. The tubes are well shaken and immediately placed in a water-bath at 80° and kept therein at this temperature for 15 minutes. Until this method of manipulation was adopted, it was difficult to obtain agreeing results when duplicate tests of known solutions were made.

474. Method for the Determination of Nitrous Nitrogen.—After trials of various methods the naphthylamin and sulfanilic acid method was adopted. The method of manipulation is substantially that in use in water analysis with several important modifications which will be described. The principal difficulty arises from the fact that in the latter part of the culture period of eight weeks the quantity of nitrites developed by many of the soils is so great that in some of the solutions the color produced is very deep and even results in the production of a precipitate. This difficulty is obviated by the following method of manipulation.

Two and one-half cubic centimeters of the culture fluid are transferred to a graduated cylinder by means of a sterilized measuring pipette. A large quantity of distilled water is kept at hand to which has been added the proportion of naphthylamin, sulfanilic and acetic acids usually employed in the determination of nitrites in water. The portion of culture fluid contained in the graduated cylinder is diluted at first to about 100 cubic centimeters and the dilution continued as the color develops, being conducted more rapidly in the case of those tests which show the presence of greater amounts of nitrous nitrogen.

The standard solutions for comparison containing known quantities of nitrous acid are prepared simultaneously with the unknown solutions. At the end of 20 minutes or half an hour the observation is begun and is conducted in 50 cubic centimeter nessler cylinders, the comparison being made by means of transmitted light. A comparison camera similar to those used in iron and steel laboratories for carbon determinations is employed. The total volume of the solution and the number of the standard tube which matches a given unknown solution are recorded and the process is complete with the exception of the calculation.

It will be noted that acetic acid is used as the acidulating re-

agent for this test. Moderately strong acidulation is required to prevent precipitation of the colored reaction product, particularly when the color is very dark. Strong acidulation with acetic acid is found most satisfactory for this purpose.

475. Method for the Determination of Nitric Nitrogen.—For this determination a modification of the picric acid method is employed. Phenol-sulfonic acid is used, prepared according to the direction of Gill.⁵⁴ The culture medium contains only traces of chlorin, therefore precautions are unnecessary to eliminate errors arising from the presence of this substance. The test is conducted as follows:

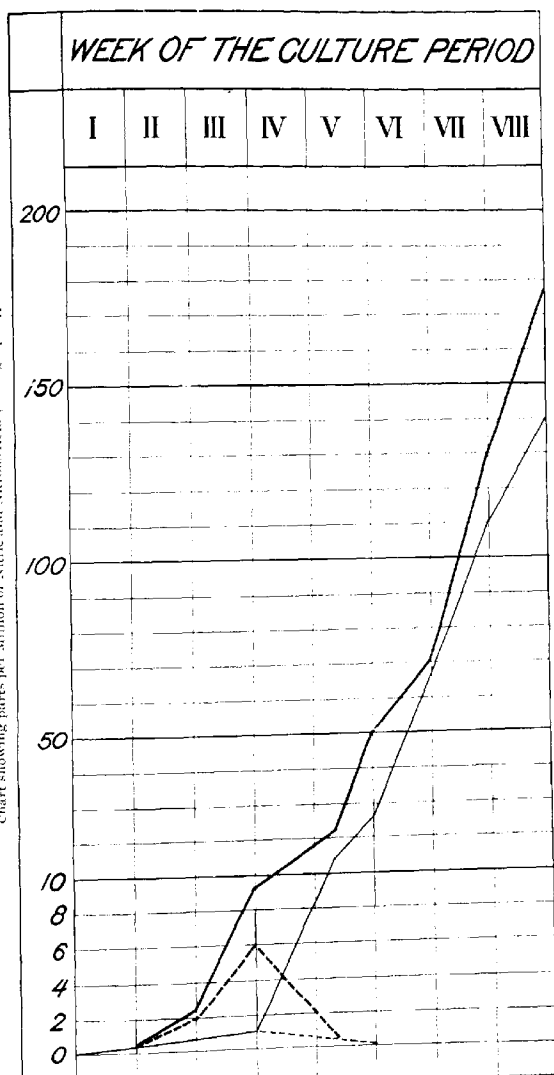
Two and a half cubic centimeters of culture liquid are transferred to a small porcelain dish by means of a sterilized measuring pipette. One drop of sodium carbonate solution is added, and the liquid evaporated to dryness. The residue is treated with the proper quantity of phenol-sulfonic acid reagent which is brought in contact with every part of the residue by means of a short stirring rod. Ten cubic centimeters of water and three cubic centimeters of strong ammonia water are added, and the unknown solutions are compared in a nessler cylinder with a standard solution prepared at the same time. Any suitable colorimeter may be used for this comparison.

476. Statement of Results of the Investigations.—In most cases the agreement in the rate and magnitude of the nitrification is very satisfactory. Any difference in the mean results from two different soils may, therefore, be attributed to original differences in the soil *in situ*.

In the sample supplying the data in the accompanying chart, it is seen that nitrification has only just commenced at the end of the first period of seven days, the quantity of nitrous and nitric acids present being, approximately, a half of one part per million in each of the duplicate samples. The first sample, represented by the heavier continuous line, shows a more marked nitrification at the end of the second week, the total quantity of nitrous acid present being two parts per million, and the total quantity of both

⁵⁴ Determination of Nitrates in Potable Water. Journal of the American Chemical Society, 1894, 16 122; Mason, Examination of Water, 1899: 43-44.

Chart showing parts per Million of Nitric and Nitrous Acids, Paragraph 476.



acids being, approximately, $2\frac{1}{2}$ parts per million. A duplicate sample meanwhile shows a total nitrification of only about one part per million. At the end of the third week the nitrous acid has risen in the first sample to six parts per million, and the two acids to a little more than nine parts per million, showing, approximately, the presence of three parts per million of nitric acid and six parts per million of nitrous acid in the first sample, while the second sample has only still a little over one part per million of nitrous and nitric acid. At the end of the fourth week the nitrifying ferment begins to gain upon the one producing the nitrous acid, both in the original and duplicate sample. In the original sample the nitrous acid has fallen to two parts per million, while the total acids have risen to almost eleven parts per million, showing nearly nine parts per million of nitric acid. In the duplicate sample there is approximately a half part per million of nitrous acid and eight parts per million of both acids, showing $7\frac{1}{2}$ parts per million of nitric acid. At the end of the fifth week the nitric ferments have gained a distinct victory. They have consumed all of the nitrous acid which has accumulated and convert any which is still formed at once into nitric condition. The original sample shows 50 parts per million of nitric acid and no nitrous acid. The duplicate sample shows 25 parts per million of nitric acid and no nitrous acid. From this point up to the close of the experiment at the end of the eighth week there is no accumulation of nitrous acid whatever, and the nitrification in the two samples progresses almost at the same rate. At the end of the period the original sample has 170 parts per million and the duplicate sample 140 parts per million of nitric acid.

477. Effect of Acidity on Rate of Nitrification.—In connection with the above investigations a study of the effect of acidity on the speed of nitrification was conducted.⁵⁵ The studies were made on 22 virgin and 22 cultivated soils from 22 States and Territories.

The following results were obtained:

⁵⁵ Ewell and Wiley, *Journal of the American Chemical Society*, 1896, 18:475.

SUMMARY OF RESULTS.

In 5 cases	0	part	per	million	of	nitrogen	was	nitrified
In 1 case	11	parts	"	"	"	"	were	"
In 2 cases	14	"	"	"	"	"	"	"
In 4 "	15	"	"	"	"	"	"	"
In 5 "	18	"	"	"	"	"	"	"
In 10 "	20	"	"	"	"	"	"	"
In 5 "	22	"	"	"	"	"	"	"
In 6 "	25	"	"	"	"	"	"	"
In 1 case	28	"	"	"	"	"	"	"
In 1 "	40	"	"	"	"	"	"	"
In 1 "	42	"	"	"	"	"	"	"
In 1 "	70	"	"	"	"	"	"	"
In 1 "	130	"	"	"	"	"	"	"
In 1 "	170	"	"	"	"	"	"	"

Averages : Of 44 tests 28 parts per million of nitrogen were nitrified

" Of 34 " 20 " " " " " " " "

In general, it was noticed that where the acidity was sufficient to consume per liter from three to four cubic centimeters of normal alkali, nitrification stopped. The quantity of nitric acid produced was in general proportional to the carbonates in the sample. The two showing 130 and 170 parts per million are samples from Alabama, containing considerable quantities of carbonate of lime. These data show the great importance of the function of carbonate of lime in nitrification in the soil.

Burri and Stutzer have found that the organisms from different soils assumed an almost uniform nitrifying power after a number of cultivations in an artificial medium.⁸⁶ This fact leads to the suggestion that valuable data would be obtained by inoculating the sterilized soils with the same organism and noting the results over long periods.

478. Occurrence of Nitrifying Organisms.—According to the observationst of Schlösing and Müntz the nitrifying organisms are widely distributed.⁸⁷ Arable soil containing considerable humus seems to be the medium in which they grow most freely and in which they accomplish their most important functions. Sewage waters are also rich in nitrifying ferments; and, in fact, all waters containing organic matter. They are also found in running

⁸⁶ Central-Blatt für Bakteriologie, 1896, 2 : 105.

⁸⁷ Comptes rendus, 1879, 89 : 891.

waters but not in great numbers. They affect chiefly the surface of bodies, and especially are found on the bottom of culture-flasks.

These authors have not found the nitrifying organisms in normal air. They could not seed sterilized flasks with nitrifying organisms by admitting air freely. The absence of these ferments from the air is explained by reason of their sensitiveness to desiccation.

The method used by Schlösing and Müntz for the separation of the organism consisted in the preparation of original and subcultures in sterilized solutions containing nitrifiable matters. The proof of isolation was assumed when a given subculture contained only one kind of organism as seen with the microscope. The appearance of this organism, as described by the authors, was that of the later isolations by Warington and Winogradsky, but the method used could hardly now be regarded as decisive.

479. Warington's Culture Medium.—The solution recommended by Warington for the culture and isolation of the nitrifying ferments has the following composition:

	Milligrams
Ammonium chlorid.....	80
Sodium potassium tartrate.....	80
Potassium phosphate.....	40
Magnesium sulfate.....	20
Calcium carbonate, in excess, about.....	200
Pure bacteria-free water, to make one liter.	

480. Apparatus and Manipulation.—The experiments are conducted in short, wide-mouthed bottles. The initial volume of the solution in each bottle is 100 cubic centimeters, and the bottle should be of such size as to give a depth of liquid of from three to five centimeters.

The neck of the bottle is closed with a plug of cotton and this is protected from dust by tying over it a cap of filter paper. Arranged in this way, filtered air has free access to the solution. The bottle with the solution thus protected is placed in a water-oven and kept near the temperature of boiling water for from six to eight hours to destroy any organisms present. When cool, the solution is ready for use.

The calcium carbonate used should be prepared by precipitation and added in a moist state. The calcium carbonate solution should be added after the sterilization of the liquid, the precipitated carbonate being boiled just before it is added.

Preparation of Seed.—The seed employed to start the nitrification should be a small quantity of fresh soil, usually about one-tenth of a gram. If a previously nitrified solution be used for seed it should be thoroughly shaken and about one cubic centimeter of the solution removed for seeding the new bottle.

In introducing the nitrifying liquor into the bottle the plug should be lifted slightly and a small pipette inserted by means of which the liquor is added. The operation should be carried on in a room perfectly free from dust and to which no one but the operator has access. The greatest care should be exercised to prevent any particles of matter entering the solution except that which is purposely added. In withdrawing the liquor from the nitrifying solution, cotton wool should be pressed around the top of the pipette so that the entering air may be filtered before admission to the interior of the bottle. The pipette which is used should be kept in boiling water until it is required for use. After use it should be washed and replaced in boiling water until again required.

After seeding, the bottles should be placed in a dark cupboard and exposed to the ordinary temperature of the laboratory. If a higher or stated temperature be desired, the bottle should be placed in a metal box the temperature of which can be regulated to any degree.

Test of the Commencement of Nitrification.—The beginning of the nitrification can be determined in a solution by testing it with diphenylamin. One cubic centimeter of the solution withdrawn as above indicated, is placed in a small beaker, a drop of solution of diphenylamin sulfate in sulfuric acid added, and then two cubic centimeters of concentrated sulfuric acid and the contents of the beaker well shaken. The development of a violet-blue color shows the presence of nitric or nitrous acid. This test will detect one part of nitric nitrogen in 20 millions parts of water.

Determining the Progress of Nitrification.—The progress of

nitrification is determined by repeated examinations for ammonia by nesslerizing, and for nitrous acid with metaphenylenediamin. Each experiment is made with five cubic centimeters of the solution withdrawn as above indicated and placed in test-tubes, always of the same size. The reaction with the nessler solution is then made by adding it in the usual way. The colorations are recorded as, trace, small, moderate, considerable, large, and abundant.

If the change produced by the organism consisted in the formation of nitrites only, the ammonia in the original solution would fall from *large* to *trace*, while the nitrous acid would increase from *trace* to *large*. If the nitrification consisted in the production of nitrates only, the ammonia would diminish without any corresponding production of nitrous acid. In mother solutions which contain ammonium carbonate instead of sulfate, it should not be forgotten that the ammonia might gradually disappear owing to the volatilization of the carbonate without any corresponding production of free nitrites or nitrates. The total disappearance of the ammonia in the above experiments shows the completion of the process.

481. To Determine the Distribution of the Nitrifying Organism in the Soil.—The principle on which the determination of the distribution of the nitrifying organism in the soil depends, rests upon seeding the growth solutions with samples of soil taken at different depths and carefully protected from the time of sampling until the time of seeding from any admixture of accidental organisms. The method of study used in the Bureau of Chemistry has already been described.

The method of Warington is described below.⁵⁸ The samples of soil are secured by digging a pit of convenient depth usually from eight to ten feet. A fresh surface is then cut on one of the sides of the pit at the spot selected for sampling. This surface is scraped with a freshly ignited platinum spatula. The spatula should then be washed, re-ignited, and cooled, and a small portion of the soil, at the depth required, detached with the spatula and

⁵⁸ Journal of the Chemical Society (Trans.), 1884, 45 : 645.

transferred at once into one of the growth bottles already described.

The growth solution best suited for the purpose contains four cubic centimeters of urine per liter. Each bottle should also contain some freshly precipitated calcium carbonate. In sterilizing urine solutions the calcium carbonate should be added before the heating instead of afterwards. The quantity of soil taken for each seeding should be about one-tenth of a gram.

Inasmuch as the cotton stopper has to be lifted to introduce the soil, opportunity is given for the entrance of any organisms floating in the air. Experience, however, has shown that air free from soil dust very seldom contains nitrifying organisms. The seeded bottles are placed in a dark cupboard of moderate temperature as already described.

482. Sterilized Urine Solution.—The sterilized urine solution used for the determination of the distribution of the nitrifying organisms in the soil, is made by diluting four cubic centimeters of healthy urine to one liter, adding some freshly precipitated calcium carbonate, stoppering with cotton wool and heating for several hours at the boiling temperature of water.

As a result of Warington's experiments it was shown that the nitrifying organism in the soil did not exist, at least in portions of one-tenth of a gram, to a greater depth than 18 inches. In only one case was nitrification produced from a sample of soil taken at a greater depth and this may have been due to the accidental introduction of organisms from other sources. It may be assumed that any long delay in the commencement of nitrification under favorable conditions, implies the presence of a very limited quantity of organisms in the solution. Thus a comparative study of the period of incubation and the progress of nitrification in solutions seeded with soils taken at different depths or at different places, becomes a fair index of the number and vitality of the nitrifying organisms contained therein.

483. Depth to Which Micro-Organisms are Found.—As seen above, Warington found very few organisms below 18 inches. Koch states that at the depth of about one meter, the soil is nearly free from every kind of bacteria.⁵⁹ These observations have been

⁵⁹ Jahresbericht über die Agrikultur-Chemie, 1881, New Series, 4 : 43.

corroborated by other observers, and by the author's experience, and it is now believed that not many active bacteria are found in soils to a greater depth than about three meters.

It is evident from the nature of the experiments above described that the nitrifying processes go on almost exclusively in those portions of the soil which are subject to cultivation, while in the subsoil and below the processes of nitrification are either retarded or arrested. Any stores of nitrogenous matter, therefore, in an insoluble state, resting in the subsoil, are preserved from oxidation and consequent waste until such time as they may be removed to near the surface.

484. Isolation of the Nitrous and Nitric Organisms in the Soil.—

The action of the organisms which produce nitrification either in form of nitrites or nitrates, having been thoroughly established, and the method of testing the soil therefor given, it remains to describe a method by means of which these organisms in the soil may be isolated and obtained in a state of purity. The difficulties attending this process are extremely great on account of the similarity of the two organisms. The first attempts to make pure cultures of the two separate organisms were attended with but little success. Following the brilliant researches of Winogradsky the technique of the process has been greatly improved by many workers. It is not desirable here to trace the later development of these methods but rather to give a brief description of the earlier investigations which are most valuable from an historical point of view and because they so well illustrate the principles on which the investigation rests.

According to Winogradsky the method of culture on gelatin so long practiced is not to be relied upon.⁶⁰ It is not difficult to eliminate by this process the organisms which grow rapidly in gelatin and which mature their colonies in two or three days, but where they require from eight or ten days to produce a colony the method is unsuccessful. In fact, by the gelatin process as it was at first practiced, much was owing to chance, but sometimes by a happy accident a pure nitro-bacterium might be isolated.

Formerly it was considered that a liquid could be regarded as sterile if it gave no growth upon gelatin. It has, however, now

⁶⁰ *Annales de l'Institut Pasteur*, 1891, 5 : 92.

been demonstrated that a liquid may contain large numbers of nitro-bacteria and still produce no growth upon gelatin. However, for the organisms which accompany the nitro-bacteria in soils, it is regarded as certain that if no growth on gelatin is produced by them they are absent. Therefore in the case of a solution which has been seeded with a soil, if it can be brought to such a state as to produce no growth on gelatin, it may be safely assumed that it contains no bacterial organisms save those which are capable of producing nitrites or nitrates. Therefore, if such a solution produce nitrification and at the same time no growth upon gelatin, it may be considered as a proof of the isolation of the nitro-organisms from all others.

This method was also worked out independently by Percy and Grace Frankland.⁶¹

These views are provisionally advanced and are not regarded as definitely established. Strictly speaking, the proof of seeding gelatin is not sufficient alone because the absence of growth can not be regarded as the exclusive privilege of the nitro-bacteria. Such might be the case sometimes for an accidental mixture of microbes, introduced with any given sample of soil into the cultures, but the criterion is not absolute. Microbes, for example, of a sulfurous or ferruginous nature may be cited, for which the gelatin layer is not only unfavorable but even fatal. It may thus happen that there may be eliminated from the solution all that will grow upon gelatin without freeing it from some special kinds of cultures, refractory like the nitro-bacteria, but which might reappear if they should be resown in some favorable nutritive solution. On account of this fault in the process, Winogradsky has been impressed with the necessity of bringing out a better method.

In using the gelatin media it is necessary to find the one that is suited to nourish these organisms, which would evidently be the way promising the greatest success. This having been found, and those organisms which produce colonies being easily recognizable, a great step towards the solution of the problem will have been made and the more so as the medium would be at the same

⁶¹ Philosophical Transactions of the Royal Society, 1890, 181 : 107.

time absolutely unfavorable to other forms of microbes. On account of the slow degree of development of the nitro organisms, all others would probably have opportunity to grow and strengthen to their exclusion, unless these interfering organisms could be completely removed.

485. The Culture Solution.—The culture-solution, first proposed by Winogradsky, has the following composition:

To ten grams of gelatin or one part of agar-agar in 100 cubic centimeters of water add one-tenth of a gram of potassium phosphate, five-hundredths of a gram of magnesium sulfate, a trace of calcium chlorid, and half a gram of sodium carbonate. The solution being sterilized in the usual way by heating, there are added to it a few cubic centimeters of a sterilized solution containing two-tenths per cent of ammonium sulfate. Although such a solution has been supposed to be very favorable to nitro-organisms, no definite results were obtained.

The non-success of this method led Winogradsky to adopt a nitrifying solution which absolutely excluded all organic substances. Instead of using an animal or vegetable gelatinous substance he used one of a mineral nature, first proposed by Graham and developed by Kühne⁶². Two of these gelatinous mineral substances were considered; *viz.*, the aluminum hydroxid and the hydrate of silica. The latter was finally chosen.

486. Preparation of the Mineral Gelatinous Solution.—The soluble glass which is found in commerce is generally of a thick, sirupy consistence. It is first diluted with three times its volume of water. One hundred cubic centimeters of this liquid are poured with constant stirring into 50 cubic centimeters of dilute hydrochloric acid and the mixture placed in a dialyzer. It is useless to employ a standard solution of silica. All that is necessary is to submit to dialysis a liquid with an excess of acid and sufficiently dilute not to be exposed to the danger of being spontaneously gelatinized in the dialyzer. The dialyzer is left for one day in running water and two days in distilled water, often renewed. The solution is ready for use when it is no longer rendered turbid on the addition of silver nitrate, showing that the

⁶² Zeitschrift für Biologie, 1890, New Series, 9 : 172.

hydrochloric acid (sodium chlorid) has been entirely extracted. The solution is sterilized by boiling, and preserved in a glass flask closed with a plug of cotton.

More recent instructions by Winogradsky for preparing the gelatinous silica recommend dialyzing the soluble glass after treatment with hydrochloric acid in a parchment tube.⁶³ The proportions of silicate and acid are 100 cubic centimeters of the silicate solution (1.06 specific gravity) and 100 cubic centimeters of hydrochloric acid (1.1 specific gravity). With a dialyzing tube placed two days in running water and one day in distilled water frequently changed it will be found that the acid is completely removed. One hundred cubic centimeters of the residual liquor giving no reaction for hydrochloric acid are concentrated to 20 cubic centimeters. When cold there is added one cubic centimeter each of a solution of ammonium sulfate and of sodium carbonate, together with corresponding quantities of the other nutrient salts commonly employed. The ammonium sulfate should never exceed from two to two and a half, and the sodium carbonate four parts per thousand. To the flask containing the above substances is added one drop of the seed-liquor, which may be a soil water or a drop from some previous culture. The flask is shaken and the mixture poured into a low circular glass dish which is covered by one slightly larger in diameter (Petri double dish). To the liquid in the dish is added a drop of a cold saturated solution of common salt, and it is then stirred with a platinum spatula. The addition of the salt greatly favors the setting of the jelly. The jelly may set in from two to three hours, but a longer time secures better results in the end.

In employing these preparations as seed, after the organisms have grown, it is absolutely necessary to use the isolated cellules and not the aggregated masses (zoöglææ). The latter are rarely free of foreign germs which adhere to their gelatinous envelope. Since the zoöglææ can not be broken up by any artificial means it is necessary to await their spontaneous disintegration in order to separate the mobile monads. The opalescence of the culture-liquid is a sure index of this separation.

⁶³ Archives des Sciences biologiques à St. Pétersbourg, 1892, 1 : 107.

The particles of mineral gelatin to be used as seed for nitrifying are best taken as follows:

A glass tube is drawn out immediately preceding the operation, until the end is as fine as a hair. The surface of the mineral gelatin is magnified by means of a dissecting microscope and the preparation table is so arranged as to give a perfect support to the right hand which should hold the filament of glass. The smallest colony is then pricked with the needle and the end of the glass is broken and dropped into the flask which is to be seeded. The seed is thus selected in as small a particle as may be desired, only a few cells, but it can always be ascertained with certainty that some of the particles have been obtained by this operation.

The method of cultivation on mineral jelly is considered by Winogradsky an important resource in the study of the nitrifying organisms. It removes the chief difficulties heretofore existing in discovering and characterizing these organisms among the innumerable micro-organisms of the soil. The long series of cultures necessary to separate the organisms are rendered unnecessary. By directly introducing a little of the earth into the silicic jelly the active organisms in nitrification can be at once discovered. It is preferable, however, as indicated below, to previously produce a nitrification in an aqueous solution by a trace of earth and to take from it the seed for impregnating the solid medium. In order to show at once a proof of its nitrifying character, it is only necessary to take a small bit of the mineral jelly, the size of a grain of rye, and to throw it into a little sulfuric acid which has been treated with diphenylamin. There is at once formed a blue spot equal in intensity to a saturated solution of anilin blue.

In regard to the growths which nitro-organisms make in a medium of the kind described, they are far from being so marked as are those produced by ordinary micro-organisms.

A nitro-bacterium is not capable of the energy of growth which is recognized for the greater number of microbes. The colonies contained in the gelatin always remain small. The largest among them are just visible to the naked eye like white points. Along the striae, on the contrary, there is formed quite a thick white crust. To the naked eye, in general, there is nothing very char-

acteristic in the formation of colonies in a medium of this nature. But this impression changes altogether when the plaques are examined with a low magnifying power. The colonies, especially those of the interior surface, reveal then an aspect so curious as to be well remembered when once seen.

This mineral gelatin, as has already been noticed, is very unfavorable to the growth of microbes other than nitro-bacteria and becomes altered only under the action of the air. If the plaques be carefully preserved from desiccation the culture of these organisms can be continued for several weeks. Although they do not seem to increase, the colonies, as well as the jelly, are still in a good condition at the end of that time. Nevertheless the expectation that this medium would prevent the formation of any foreign organism has not been realized. Some of the organisms which accompany the nitro-bacteria in soil, also grow upon the silicic jelly; but they do not form colonies, properly so-called, and their growth is extremely slow. They generally make their appearance before the nitro-bacteria and spread exclusively upon the surface in form of white spots, so transparent that without careful examination they would not be discovered. Having reached a certain size the spots do not change during entire weeks. This circumstance renders the operations of isolation somewhat delicate, but does not prevent them.

487. Preparation and Treatment of the Solution to be Nitrified.—The organisms having been grown on the siliceous gelatin in the manner described they are tested for their nitrifying power as follows:

The mineral solution which is to be nitrified with the above preparation is composed of four-tenths gram of ammonium sulfate, half a gram of magnesium sulfate, one-tenth gram of potassium phosphate, a trace of calcium chlorid, six-tenths to nine-tenths gram of sodium carbonate, and 100 cubic centimeters of distilled water.

The sulfates with the calcium chlorid on the one hand, and the phosphate and carbonate on the other, are dissolved separately and the two solutions sterilized separately and mixed after cooling. The seeding is then done as described above.

488. Isolation of the Nitrous and Nitric Organisms.—Instead of proceeding immediately to the isolation of special organisms in the soil, the preliminary period of purification is prolonged by Winogradsky by allowing the free growth of all the organisms which can be maintained in the ordinary medium.⁶⁴

The composition of the culture solution employed is as follows: One thousand parts of distilled water, one part of potassium phosphate, half a part of magnesium sulfate, and a trace of calcium chlorid. Each flask receives besides this some magnesium carbonate, freshly washed with boiling water and added in slight excess.

The flasks thus charged are sterilized, and there are added two cubic centimeters of a solution of two per cent of ammonium sulfate, which when added to 15 or 20 cubic centimeters of liquid give from two to two and a half parts per thousand. They are then seeded with soil. The reasons for this preliminary treatment are as follows: First, all the observations upon the enfeeblement of the oxidizing power of these organisms have been made upon cultures seeded simply by the fresh soil, and in cultures derived therefrom. In the second place, the existence of the two forms, one nitrous and the other nitric, prevents at once the isolation of a single organism.

Samples of soil from Europe, Africa, Asia, Australia, and America, were used for seed in the experiments. First, the cultures were made by seeding with a small quantity of each of these samples of soil, and each one of these cultures served at a point of departure for a series of subcultures. The temperature of the cultures should be kept constantly at 30°.

The method of following the nitrification adopted by Winogradsky is essentially that of Warington, the percentage of ammonia remaining at any time being determined by nesslerizing. To detect the presence of nitric acid the nitrous acid is decomposed by boiling with ammonium chlorid in excess, or with area, and then diphenylamin is used as a reagent. By treatment with ammonium chlorid and boiling, the ammonium nitrite is resolved into free nitrogen and water as indicated by the equation

⁶⁴ *Annales de l'Institut Pasteur*, 1891, 5 : 577.

$\text{NH}_4\text{NO}_2 = \text{N}_2 + 2\text{H}_2\text{O}$. Or the total oxidized nitrogen may be estimated by the Schlössing method or by any of the standard methods hereafter given. The nitrous acid is then determined by potassium permanganate and the nitric acid by difference.

A great difference is to be noted between freshly taken earth and that which has been kept for a long while, especially when sealed. With fresh earth from near the surface a mere trace is sufficient to produce nitrification. With samples of earth which have been kept for a long while and thoroughly dried, several grams must be added in order to secure perfect nitrification. The period of incubation with the samples of earth ranges from three to 20 days. The beginning of the phenomenon is revealed by the appearance of nitrous acid, of which the quantity is increased very rapidly, but in the end it disappears and is transformed into nitric acid.

489. Statement of the Results.—The method of stating the results of examination of soils for nitrifying organisms conducted as above is illustrated by the following example:

Soil from Zürich.—The culture was seeded on the 11th of October, with one gram of soil. On the 20th of October the nitrous acid had reached its maximum of intensity and there was no ammonia left. On the 29th of October the nitrous acid remained almost stationary and there was hardly any nitric acid present. On the 1st of November the reaction for nitrous acid began to decrease. On the 5th of November the reaction for nitric acid was very intense. On the 11th of November the nitrous acid had all disappeared except a mere trace.

The above order of phenomena was observed with all the samples of soil tried, from which it is concluded with certainty that nitrifying organisms transplanted directly from their natural medium in the soil into a liquid easily nitrifiable produce at once nitrous acid in abundance. The phenomenon of nitrification is divided into two periods therefore, of which the first is devoted to the production of nitrites, and the second consists in the oxidation of the nitrites, and this does not commence until the total disappearance of the ammonia. Occasionally the formation and oxidation of the nitrites practically go on together, but never equally,

the oxidation of the nitrites being always sensibly behind their formation.

490. Method for Subcultures.—From the mother cultures described above, Winogradsky makes subcultures as follows:

The solution to be nitrified is prepared as in the mother cultures. The seeding is accomplished by adding a small quantity of the liquor of the mother culture after shaking. Subcultures can be made in this way to the seventh generation.

In respect of the oxidation of the nitrites the results may be entered as negative if they have not disappeared at the end of two months.

To determine whether the process of oxidizing the nitrites is in progress or not the total nitrous acid is estimated, and the process repeated at the end of eight or ten days. Should there be no diminution of the nitrous acid within this time it may be considered that the further oxidizing action is not taking place.

491. Use of a Solid Medium.—It may be justly claimed that the action of nitrifying organisms in a liquid is not to be compared with their action in a solid medium, such as a soil which is their natural habitat. It might be, therefore, that the inability of the nitrous organism to produce nitrates is due to the nature of the medium in which it is cultivated. Winogradsky in order to determine this question cultivated the organism in a solid medium of two kinds, first a silicate gelatin impregnated with an ammonium salt and second in sterilized earth. The silicate jelly is prepared as follows:

Mix a jelly of silica containing some ammonium sulfate with sterilized soil. The seeding is done with one of the subcultures which no longer has the power of producing nitrates.

In the case of the jelly the seeding is accomplished as follows:

A minute drop of a culture liquid is taken with a capillary glass tube and applied in striæ to different parts of the solid jelly; or a minute drop of the culture liquid may be mixed with the jelly before solidification. The Petri dishes in which these cultures are made can be preserved in a moist atmosphere, and thus the desiccation be easily prevented for a long time. From time to time

pieces of the jelly as large as a pea can be tested for the progress of nitrification.

Results.—The nitrous reaction, both in the prepared jelly and in sterilized soil, will appear in a few days. At the end of from seven to 12 days it will have attained its maximum intensity and will then remain stationary indefinitely. Sterilized soil has no power to generate the nitric from the nitrous ferment. The two organisms are, therefore, of different species.

After a few generations the power of producing nitrates seems to be lost although the nitrous ferment may still be active. This suppression of the power to oxidize the nitrites is not due to any pernicious influence of the culture-medium but to the condition of the successive solutions at the time of removing the seeding samples.

492. Microscopic Examination.—A small particle of the deposit in the culture-liquid is spread on a glass slide and dried. There is then added a drop of very dilute perfectly transparent malachite green solution; the zinc chlorid double salt or oxalate of bitter-mandelölgrün, or tetramethyldiamidotriphenylcarbinol. In about half a minute it is washed and colored by a very dilute solution of gentian violet which is left to act for some time. The cells then appear distinctly colored on a colorless background.

In examining nitrous cultures in this way under a moderate enlargement there are seen particles of material covered with scattered groups and massive zoöglææ composed of cells which are, doubtless, identical.

By their round or roundish forms, by their relative size and especially by their numbers and uniformity they are at once distinguished from the other vegetations which are generally of a purely bacillus shape.

With the exception of some shreds of mycelium coming from some oidium in the soil the microscope reveals nothing but the organisms described. The microscopic appearance⁶⁵ of the nitrous ferment is shown in Fig. 85a.

The general conclusions of Winogradsky are:

⁶⁵ *Annales de l'Institut Pasteur*, 1891, 5 : 576, Plate XVIII.

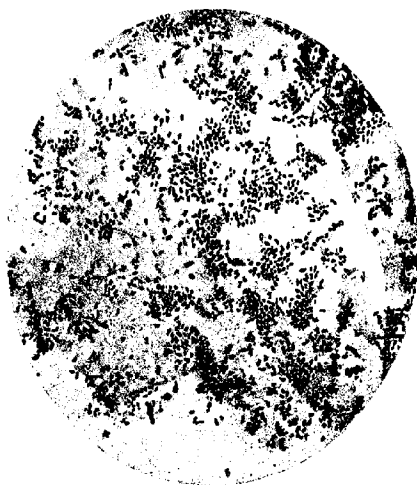
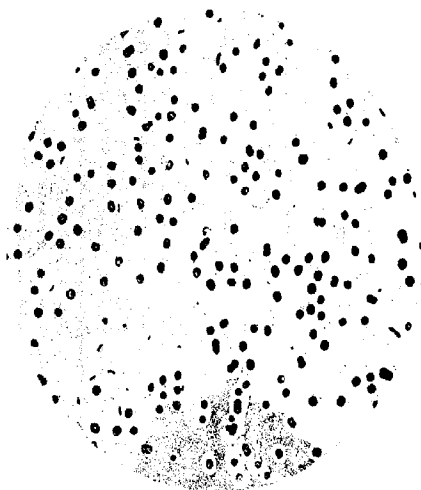


Figure 85a. (Upper figure.) Nitrous ferment prepared by Winogradsky from soil from Cito
 Figure 85b. (Lower figure.) Nitric ferment prepared by Winogradsky from soil from Cito

1. Each soil possesses but one organism capable of oxidizing ammonia.

2. Soils from one locality have always the same kind of nitrifying ferment.

3. Soils from different and distant countries contain nitrifying organisms which differ from one another in some respects so much so that it may be necessary to distinguish a few species or even genera in these bodies.

493. Isolation of the Nitric Ferment in Soils.—The principle of the separation of this ferment as described by Winogradsky rests upon the fact that in culture solutions of a mineral nature free from ammonia the nitrous ferment will not grow, whereas if nitrite or nitrous acid be present the nitric ferment will grow.⁶⁶ In a few generations, therefore, the nitrous ferment will be entirely eliminated.

Solution employed:

	Grams.
Distilled water.....	1,000
Potassium phosphate.....	1
Magnesium sulfate.....	0.5
Calcium chlorid.....	trace
Potassium nitrite.....	0.22

To culture-flasks containing 100 cubic centimeters of the above mixture after sterilization about one-tenth gram of fresh soil is added. In favorable conditions the nitrous acid will disappear in about 15 days.

Subcultures are made by seeding fresh portions of the sterilized solution with one or two cubic centimeters of the mother culture. The operation is continued until the nitrous ferment is eliminated.

The organisms in the deposit in the culture-flasks are then subjected to microscopic examination in the manner already described for the nitrous ferment; or proceed as follows:

494. Culture on Solid Media.—Evaporate the liquid which has been employed in the culture of a nitrous ferment to one-third of its bulk. Gelatinize the residue by adding double its volume of the silicic acid solution prepared as already directed.

The jelly is placed in the glass vessels usually employed. The

⁶⁶ *Annales de l'Institut Pasteur*, 1891, 5 : 596.

seeding may be done with a few drops of a culture-liquid containing the nitric ferment as obtained above. The first reaction will appear in from eight to ten days. In about 45 days the nitrous acid in the jelly will have entirely disappeared. Two classes of colonies are noticed under the microscope. The first to appear are small colonies which never extend beneath the surface of the jelly. In cultures seeded with these colonies there is no oxidation of nitrous acid. The second class of colonies extends into the interior of the jelly. They are much larger than the first, of a yellowish-gray color and not spherical but rather lenticular in shape. Cultures seeded with these colonies will lose their nitrous acid in about ten days or two weeks.

The growth of these organisms in a liquid scarcely merit the name of cultures. The naked eye can usually distinguish no form of vegetation. The liquid remains clear, the surface is free from any film, no flocks are deposited. Colored and examined in the microscope the organisms found are so puny as to make doubtful their oxidizing power. There is an apparent contradiction between the powerful chemical action that these organisms can produce and their apparent deficiency in physical properties.

These organisms are best found by cultivating them in a very limpid solution. The bottoms of the culture boxes will be found covered with an extremely tenuous gelatinous deposit communicating to the glass a feeble grayish-blue tint. The culture bottle is inclined and the bottom scratched with a recently drawn-out capillary tube. The colonies rise in the tube together with a little of the liquid. The colonies are dried, mounted, and colored as already described and when examined with the microscope are found to be composed exclusively of masses of an organism of extreme minuteness.

The organism remains attached so firmly to the bottom of the culture bottle that it can be washed several times with pure water without danger of detachment and thus rendered more pure.

In old cultures which are sustained by new additions of nitrite an extremely transparent pellicle on the bottom of the flask can be distinguished. By shaking the liquid some fragments may be detached and made to float through the fluid. With a little care

and patience these flocks can be captured, mounted, and colored. Since they show the nitric organism in its natural state their preparations are of the greatest interest.

The best preparations are made by coloring with malachite green and gentian violet and then coloring again with magenta. Afterwards the preparation is washed with warm water at 50°-60° which takes almost the whole of the color from the gelatinous matter. The cells are then clearly presented colored a reddish violet on a rose background. These organisms⁶⁷ are shown in Fig. 85b.

The figure shows the cells united by a gelatinous membrane and grouped in small dense masses composed often of a single layer of organisms. The cells are generally elongated, rarely regularly spherical or oval. Their mean length does not exceed half a micromillimeter and their thickness is from two to three times less.

The difference in form of the nitrous and nitric ferments is very marked and leaves no doubt of the existence of these two forms which are as distinct as could be desired in microbic discrimination.

495. Dilution Method of Warington.—The method pursued by Warington in preparing pure cultures of the nitrifying ferment is based on the well-known principle of dilution which may be expressed as follows:⁶⁸ In a liquid containing bacterial ferments dilution may be practiced until a drop of the liquid may contain no more than a single organism of any one kind. If now proper solutions be seeded with single drops of this solution, some of them may give colonies of pure cultures of any given organism. The solution to be nitrified has the following composition:

	Parts.
Water	1000
Ammonium carbonate.....	0.25
Ammonium chlorid.....	0.50
Potassium phosphate.....	0.04
Magnesium sulfate.....	0.02
Calcium sulfate	0.02

⁶⁷ *Annales de l'Institut Pasteur*, 1891, 5, Plate XVIII, Fig. 1.

⁶⁸ *Journal of the Chemical Society (Trans.)*, 1892, 59 : 484.

The ammonium chlorid is added to prevent the precipitation of magnesium and calcium phosphates. The solution is kept in wide-mouthed, stoppered bottles to prevent the loss of ammonium carbonate, the bottles being only half full. About 100 cubic centimeters are used for each experiment. These bottles are sterilized and seeded with fresh soil in the ordinary way. They are then covered with paper caps and placed in a dark cupboard at a constant temperature of 22°.

Special Media.—A quantity of cultivated soil is exhausted of nitrates by washing with cold water under pressure. The soil is then boiled with water and filtered. The clear amber-colored solution obtained may be used instead of water in the above formula.

Solid Media.—(1) Ordinary ten per cent gelatin made with beef broth and peptone. (P)

(2) A ten per cent urine solution solidified with six per cent of gelatin. (U)

(3) A solution of one gram of asparagin, one-half gram sodium acetate, one-half gram potassium phosphate, two-tenths gram magnesium sulfate, two-tenths gram calcium sulfate, and one liter of water solidified with six per cent gelatin. (As)

Other solid media may also be employed for the purpose of favoring, as much as possible, the growth of the nitrifying organisms.

The first culture in the ammonium carbonate solution given above, is always made by seeding with a little unmanured cultivated soil. Subcultures are seeded from this mother culture by seeding new solutions with a few drops of the original. In all cases tried by Warington the subculture produced only nitrous fermentation while the original cultures produced the nitric fermentation.

496. Microscopic Examination.—The microscopic examination of the organisms formed is conducted as follows:

The cover glasses previously sterilized are placed at the bottom of the culture-flask. At the end of the nitrification the liquid is removed with a pipette and the flask and cover glasses dried at 35°. The cover glasses are then removed and stained. The microscopic appearance of the organisms obtained by the previous

cultures show masses of corpuscles usually of oval shape and having a length generally exceeding one micromillimeter. An immersion objective giving a magnification of 800 diameters is suitable for this work.

Other forms of organisms are also met, the whole series being characterized as follows:

(1) The corpuscles already mentioned. Larger ones are frequently rough in outline resembling masses of sea-sand. The smaller oval corpuscles are regular in form.

(2) Some very small circular organisms often appearing as mere points and staining much more plainly than the preceding.

(3) A few slender bacilli, staining faintly.

All the cultures obtained by the above method give abundant growth on gelatin.

497. Trials with the Dilution Method.—One part of the third subculture in the ammonium carbonate solution described above, is mixed with 500 parts of thoroughly boiled water and one drop from a sterilized capillary tube is added to each of five bottles containing the sterilized ammonium carbonate solution. In Warington's experiments one of the five bottles was found to have nitrified after 41 days. After 91 days two more were nitrified. Two bottles did not nitrify at all. All three solutions which nitrified gave growths on gelatin. The growths took place more speedily on gelatins U and As than on P.

The organisms obtained on gelatin were seeded in appropriate liquid media but no nitrification was obtained.

A subculture from solution No. 2 of the first dilution mentioned above, was diluted to one one-thousandth, one ten-thousandth, one one-hundred-thousandth, and one one-millionth. Each of these dilutions was used for seeding with five sterilized solutions of ammonium carbonate, using the method of seeding above described. At the end of 190 days not one of these solutions had nitrified.

Warington supposed that the cause of failure in the method just mentioned might be due to the alkalinity of the ammonium carbonate. While this solution could be seeded in the ordinary way with fresh earth it might be that the faint alkalinity which it pre-

sented might prevent it altogether from action when the nitrifying agent was reduced to a few organisms.

He therefore changed the solution to one of the following composition :

	Parts.
Water	1000
Ammonium chlorid	0.02
Potassium phosphate.....	0.06
Magnesium sulfate	0.03
Calcium sulfate	0.03

The solution was divided in 20 stoppered bottles which were half filled. The bottles were divided into four series, A, B, C, D, each one consisting of five bottles, and these were respectively seeded with one drop from dilutions to one one-thousandth, one ten-thousandth, one one-hundred thousandth, and one one-millionth of a second subculture of No. 3 in the first dilution series.

After 115 days, nitrification had occurred in ten of the bottles. The other ten did not nitrify at all. Each of the nitrifying solutions was spread on gelatin, P and U being employed. Growth took place far more easily on gelatin U than on gelatin P. Of the ten nitrified solutions there were three which gave no growth on gelatin U, either when spread on the surface or introduced into the substance of the jelly. There were therefore secured nitrifying solutions which did not contain organisms capable of growing on gelatin. The supposition is therefore fair that they were pure nitrifying organisms. These fresh, pure organisms had the faculty of converting ammonia into nitrous acid only and not into nitric acid.

With the organisms thus prepared a number of solutions of potassium nitrite containing phosphates and other mineral ingredients were seeded. In no case was any loss of nitrite found, which is proof that the solution contained no organisms capable of oxidizing nitrous acid. The organisms prepared as above, have the power of nitrifying organic substances containing nitrogenous bodies.

The organism isolated as described and examined under the microscope is seen to contain two forms. The first one is nearly spherical in shape, the corpuscles varying in size from mere points.

to a diameter of one micromillimeter. The form is very striking and easily stained. The second form is oval-shaped and attains a length distinctly exceeding one micromillimeter. Sometimes it is a regular oval and sometimes it is egg-shaped. This form is stained less easily than the preceding or spherical form.

498. Method of Staining.—The method of staining employed is as follows:

A drop of the culture-liquid is placed on a glass slide and mixed with the filtered stain by means of a wire. A cover glass is placed on the drop and allowed to stand for half an hour. It is then pressed down on the slide and the liquid which exudes wiped off and glue run around the cover glass. In this way the organism is stained in its own culture-fluid and can be seen in its true form without any possibility of the destruction of its shape by drying. The plate is bright and clear though colored.

If the preparation is to be mounted in balsam a drop of the culture is dried in the center of a cover glass. It is then placed for some minutes in dilute acetic acid to remove matter which would cause turbidity. The cover glass with its contents is then washed, dried, and stained for some hours in methyl violet.

499. Classification of Nitrifying Organisms.—The names proposed by Winogradsky for the various organisms are the following:

For the general group of microbes transforming ammonia into nitric acid, *Nitrobacteria*.

For the nitrous ferments of the Old World:

Genus, *Nitrosomonas*:

Species, *Nitrosomonas europaea*.

Nitrosomonas javanensis.

For the nitrous microbes of the New World:

Genus, *Nitrosococcus*.

Species, not determined.

For the nitric ferment:

Genus, *Nitrobacter*.

500. Nitrification in Sterilized Soil.—The process of nitrification in sterilized soil, when seeded with pure cultures, is determined as follows:

Preparation of Sample.—The fresh sample of cultivated soil is freed from pebbles and vegetable debris and reduced to as fine a state of subdivision as is possible in the fresh state. It is placed in quantities of about 800 grams in large crystallizing dishes.

One dish is set aside for use in the natural state, and the other, hermetically closed, is placed in a sterilizing apparatus and subjected to the action of steam for two and a half hours. This treatment is repeated three times on as many successive days.

Seeding of Sample.—Each of the two dishes is moistened with 50 cubic centimeters of pure water containing 500 milligrams of ammonium sulfate. The sterilized portion is then seeded with a preparation of the pure nitrous ferment, produced as before described. The seed is prepared by filtering a few cubic centimeters of the nitrous culture liquid through asbestos. The asbestos is well washed and then thrown into a flask containing a few cubic centimeters of sterilized water and well-shaken. The water carrying the filaments of asbestos is poured drop by drop on the surface of the soil in as many places as possible. The two dishes of soil are kept at an even temperature of 20° in a dark place. Winogradsky found that, treated in this way, the unsterilized soil produced only nitrates, while the sterilized portions produced only nitrites.⁶⁹

501. Variation of the Determinations.—To vary the conditions of the experiment Winogradsky uses 12 flasks of the erlenmeyer shape, four having bottoms 12 centimeters in diameter, and eight of them five centimeters in diameter. In each of the four large flasks are placed 100 grams of fresh soil, and in each of the eight small flasks 25 grams. The eight small flasks are designated a, b, c, d, and a', b', c', d', and the four large flasks A, B, C, D.

The flasks a, b, c, d, and a', b', c', d', are placed in a stove at 30° for several days before use, while A, B, C, D, are kept at 20°-23° for the same length of time. The soil in the small flasks is, therefore, somewhat drier than that in the large ones.

The flasks are treated as follows:

a, a', A, contain the soil as prepared above for control.

b, b', B, are sterilized at 135° and seeded with a drop of the pure nitrous culture.

⁶⁹ Annales de l'Institut Pasteur, 1891, 5 : 605.

c, c', C, sterilized as above and seeded with a little of the unsterilized earth.

d, d', D, sterilized as above and seeded with pure nitrous and pure nitric cultures.

After sterilization there are added to the small flasks two cubic centimeters of a 20 per cent sterilized ammonium sulfate solution, and to the large ones six cubic centimeters. At the end of a month or six weeks the contents of the flasks are thrown on a filter and washed with cold water until a drop of the filtrate gives no blue color with diphenylamin. The respective quantities of nitrite and nitrate are then determined in the filtrates by the usual processes, which will be fully described further along.

502. *Azotobacter* of Byerinck.—Lipman has summarized the later investigations of the active soil nitrifying organisms and studied their relations to soil fertility.⁷⁰

The entire group which is called *Azotobacter* is composed of rather vigorous bacteria producing no spores. The pure cultures grow in a great variety of media, preferably in those poor in nitrogen. They seem to be most vigorous at a temperature of 28°. Two species were isolated by Byerinck, namely, *Azotobacter Chroococcum* and *Azotobacter Agilis*. They grow on a great variety of media, particularly agar-agar, to which two per cent of acid potassium phosphate is added. They produce a green or red pigment with salts of organic acids and do not liquify gelatine.

Two additional species have been isolated by Lipman himself. A very large *Azotobacter* was named by Lipman in honor of the discoverer of the group *Azotobacter Beyerinckii*.

Lipman also describes the nitrogen fixing power of the different species. The attempts which have been made so far to utilize the *Azotobacter* species for increasing the store of soil nitrogen have not been very successful. In the experiment of Lipman it is noticed that there is no decided gain in the inoculated soils over the non-inoculated. The determination, however, of this point is far from complete, and it is not beyond the sphere of probability that this species may be found to be useful in fixing and increasing the stores of nitrogen.

⁷⁰ Twenty-fifth Annual Report of the New Jersey State Agricultural Experiment Station, 1904 : 237 et seq.

503. Fixation of Free Nitrogen.—The fixation of free nitrogen in the symbiotic activity of certain nitrifying organisms with leguminous plants is not a problem suitable for discussion, except incidentally in this manual. The great importance of this action, however, to practical agriculture is well recognized. A recent discussion of the subject by Voorhees and Lipman gives a clear view of the importance of the subject and valuable knowledge of the technique of the methods of investigation.⁷¹

A further critical study of this subject has been made by Fischer,⁷² who questions Beyerinck's classification of *A. agilis* and shows that lime is an indispensable element in the development of the *Azotobacter*, and that this element favors both nitrification and dinitrification. Lime is useful not only as a direct stimulant to nitrification, but also it is indirectly useful in promoting the production of humus which is a substance well suited to supply the *Azotobacter* with carbon.

504. Sterilization.—One of the chief requisites for success in the bacteriological investigation of soils is found in the thoroughness of the sterilizing processes. The value of cultures depends chiefly on the care with which the introduction of foreign germs is prevented. In the following description a mere outline of the method of sterilization is presented, while those who wish to study more carefully the details of the process are referred to the standard works on bacteriology.

Sterilization of the Hands.—It is important that the hands of the operator handling apparatus and materials for bacteriological work should be sterilized. The sterilization may be accomplished in the following way:

The nails are cut short and thoroughly cleaned with soap and brush. The hands are thoroughly washed in hot water with soap. After washing in hot water the hands are washed in alcohol and ether. They are then dipped in the sterilizing solution.

This liquid may consist of a three per cent solution of carbolic acid, which is the one most commonly employed. A solution of corrosive sublimate, however, is perhaps the best disinfectant. It

⁷¹ Journal, American Chemical Society, 1905, 27 : 556.

⁷² Journal für Landwirtschaft, 1905, 53 : 61.

should contain from one to two parts of the crystallized salt to 1,000 parts of water. It has lately been advised to use the sublimate in an acid solution. Acetic acid or citric acid may be employed, but hydrochloric acid is recommended as the best, in a preparation of one-half part per 1,000. For stronger solutions of sublimate containing more than a half per cent, equal quantities of common salt should be added. The solution should be made with sterilized water.

After dipping the hands in the sterilizing solution they are dried with a napkin taken directly from a sterilizing oven, where it has been kept for some time at the temperature of boiling water. Where only ordinary work in bacteriology is contemplated this sterilization of the hands is not necessary. It is practiced chiefly in antiseptic surgery. The use of thin sterilized rubber gloves on the sterilized hands is an additional guaranty of safety, and excludes many dangers from infection.

Sterilizing Apparatus.—With platinum instruments the most effective and easiest way for sterilizing is to hold them in the flame of a bunsen until they are red hot. Steel and copper instruments can not be treated in this way without injury. They are best sterilized by submitting them to dry heat in a drying oven at a temperature of 150°-160° for two hours. Glass and porcelain apparatus can be sterilized best in the same way.

All apparatus and materials employed should be used in a space as free as possible from dust, so that any germs which might be carried in the dust can be excluded from the apparatus in transferring it from one place to another.

505. Methods of Applying Heat.—Sterilization by means of heat may take place in several ways.

First. Submitting the Materials to Dry Heat Without Pressure.—The temperature in sterilization of this kind may vary from the temperature of boiling water at sea-level to 160° obtained by an oil-bath or by an air-oven.

Second. Sterilization in a Liquid Under Pressure.—This form of sterilization may be effected by sealing the liquid in a strong vessel and submitting it to the required temperature. If the temperature required be greater than that of boiling water the vessel

can be immersed in a solution of some mineral salt which will raise the boiling-point.

Third. Sterilization in Steam Under Pressure.—This method of sterilization consists in placing the body in a proper receptacle

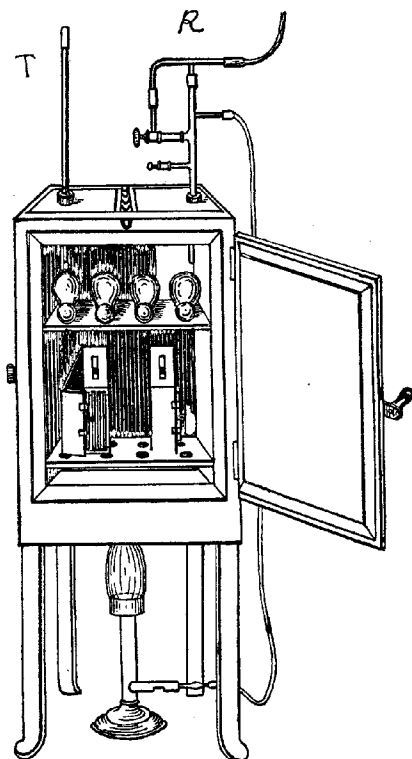


Fig. 86. Sterilizing Oven.

in vessels to which the steam can have access and then admitting steam from a boiler at any required pressure. In the case of small apparatus, such as the autoclave, the steam can be genera-

ted in the apparatus itself. The variety of apparatus used in the above method of sterilization is very great, but all the forms of apparatus employed depend upon the principles indicated.

506. The Sterilizing Oven.—The apparatus for sterilization by means of hot, dry air usually consists of a double-walled vessel made of sheet-iron, usually with a copper bottom. The apparatus is shown in Fig. 86.

The temperature is observed by means of a thermometer, *T*, and controlled by the gas-regulator, *R*. This is one of the ordinary gas-regulators by means of which the amount of gas supplied to the lamp is increased if the temperature should fall, and diminished if it should rise above the required degree. The best form of the sterilizing ovens is provided with a means for circulating the hot air so that the temperature may be made uniform throughout the mass. This can be accomplished by introducing a mechanical stirrer, or by the movement of the air itself.

Between the walls of the vessel may be placed water, provided the temperature of sterilization be not above that of boiling water. If it should require a higher temperature than boiling water, a solution of salt can be added until the required temperature is reached, or the space between the two walls may be left vacant and hot air made to circulate around the oven.

The exterior of the oven, except at the bottom where the lamp strikes the copper surface, should be protected by thick layers of asbestos or other non-conducting material. To avoid danger of flying filaments, this covering should be coated with some smooth paint which will leave an even surface not easily abraded.

507. Sterilization with Steam at High Pressure.—The apparatus used for this is commonly called an autoclave, and is shown in Fig. 87.

The top is movable and held in place by the clamp, *a*, which is held by the screw attached to the lever, *b*. The vessel itself is double-jacketed and the pressure is obtained from water in the vessel heated by means of the lamp, *c*. The actual steam pressure is indicated by the index *d*. The safety-valve, *e*, allows any excess of steam to escape above the amount required for the maintenance of the pressure. This, however, is best regulated by the lamp.

The outer jacket permits the heat from the lamp to circulate around the inner pressure vessel, and the holes near the top, *oo*, are for the escape of the heated gases. Enough water is placed in the bottom of the inner pressure vessel to supply all the aqueous vapor necessary to produce the required pressure and still leave some water in excess.

The materials to be sterilized are held on the shelves of the stand and the vessels may be of various kinds according to the nature of the material to be sterilized. The vessels containing the material being covered, the steam does not necessarily come in actual contact with it. At the end of the operation the safety-

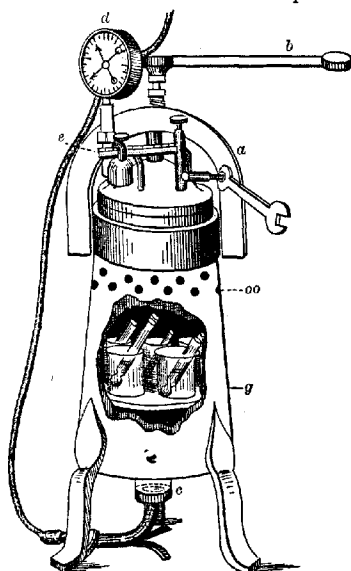


Fig. 87. Autoclave Sterilizer.

valve must not be opened to allow the escape of the steam, otherwise the remaining water would be rapidly converted into vapor and would be projected over the materials on the shelves. The lamp should be extinguished and the apparatus allowed to cook.

The autoclave is not only useful for sterilizing purposes but can be made of general use in the laboratory where heat under pressure, as in the estimation of starch, etc., is required.

These two forms of apparatus are sufficient to illustrate the general principles of sterilization by hot air and steam. There are, however, many variations of these forms designed for special use in certain kinds of work. For full descriptions of these, reference is made to catalogues of bacteriological apparatus.

508. Arnold's Sterilizing Apparatus.—A very simple and cheap steam sterilizer has been devised by Arnold.

Water is poured into the pan or reservoir, B, Fig. 88, whence

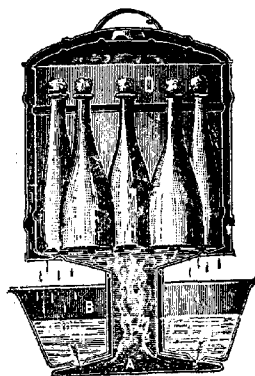


Fig. 88. Arnold's Sterilizer.

it passes through three small apertures into the shallow copper vessel, A. It is there converted into steam by being heated with any convenient lamp, and rises through the funnel in the center to the sterilizing chamber. Here it accumulates under moderate pressure at a temperature of 100° . The excess of steam escapes about the cover, becomes imprisoned under the hood, E, and serves to form a steam-jacket between the wall of the sterilizing chamber and the hood. As the steam is forced down from above and meets the air it condenses and drips back into the reservoir.

Such an apparatus as this is better suited to commercial purposes, as the sterilizing of milk, than for scientific uses.

509. Thermostats for Culture Apparatus.—It is important in the culture of micro-organisms that the temperature should be kept constant during the entire time of growth. Inasmuch as some operations continue for as much as three months or longer it is necessary to have special forms of apparatus by means of which

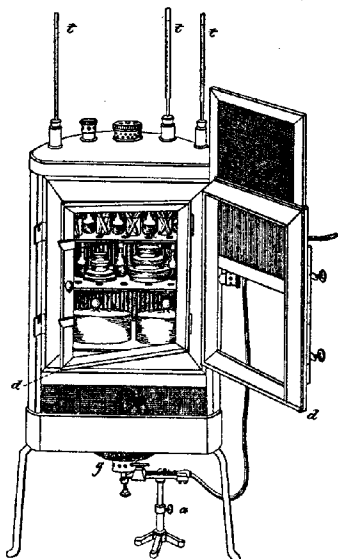


Fig. 89. Thermostat for Cultures.

a given temperature, during the time specified, can be maintained. This is secured by means of an oven with an automatic temperature regulator, practically built on the principle of the sterilizing autoclave, already described.

The essential principles of construction are, however, that the regulator for the temperature should be delicate and that the non-conducting medium surrounding the apparatus should be as perfect as possible, so that the variations in temperature from

changes in the exterior temperature, are reduced to a minimum. This delicacy is secured by introducing a drop of chloroform-ether into a confined space over the mercury of the regulating apparatus. The doors of the chamber are double, the interior one being of glass so that the exterior door can be opened for inspection of the progress of the bacterial growth without materially interfering with the interior temperature. A convenient form is shown in Fig. 89.

The apparatus figured, is oval in shape, although circular or other forms are equally as effective. The arrangement of the lamp, *a*, thermometers, *t t t*, and gas-regulator, *g*, and the double doors, *d d*, is shown in the engraving and does not require further description.

The usual temperatures for cultures range from 22° to 35°, and the apparatus once set at any temperature will remain with extremely minute variations for an indefinite time. The apparatus possesses a heat zone which, by the arrangement of the regulator, is kept absolutely constant. The space between the walls of the apparatus being filled with water, the temperature is maintained even in every part. The apparatus, as constructed, is independent not only of the surrounding temperature within ordinary variations, but also of the pressure of the barometer. Three thermometers are employed to determine the temperature of the heating zone, the water space and the inner space. The arrangement of the gas-regulator is of an especial kind, as mentioned above, by means of which the consumption of gas is reduced to a minimum. This apparatus can be regulated to suit the character of the work.

510. Microscopic Apparatus Required.—Any good microscope, capable of accurate observation, of high power, may be used for the bacteriological observations necessary to soil analysis.

Preference should be given to the patterns adapted to receive any additional accessories which may be subsequently required for advanced work. The stage, in addition to being fitted with a sliding bar, should have a large circular or horseshoe opening to facilitate focusing operations. A mechanical stage is a desirable acquisition if really well made, but a plain stage is preferable for many purposes. A rackwork, centering sub-stage is essential for

advanced work, and in the absence of the more complete form, there should at least be a fitting beneath the stage to take the diaphragm and condenser. An iris diaphragm will be found more useful than any other kind in practice, since the size of the opening can be increased very gradually at will.

One of the best lamps is known as the paraffin lamp and is fitted with a half-inch wick. This will give even more light than is actually required, and a steady flame, perfectly under control, may be obtained. For the minute details to be observed in high-grade microscopic work, such as is required in the bacteriological examination of soils, reference must be had to the standard works on bacteriology and microscopy.

511. General Conclusions.—The nitrogenous food of plants is provided in several ways; *viz.*, (1) By the nitrogen brought to the soil in rain and snow. This nitrogen is chiefly in the form of ammonia and nitric acid. The nitrogen gas in solution in rain water has no significance as a plant food. (2) By the action of certain organisms herding in the rootlets of leguminous plants, free nitrogen may be oxidized and put into form for assimilation. (3) By the action of certain organisms on nitrogenous compounds pre-existing in the soil, ammonia, nitrous acid, and finally, nitric acid, are produced. It is believed that the plant organism, unaided by the activity of a micro-organism, is usually unable to assimilate nitrogen unless it be fully oxidized to nitric acid. (4) There exist micro-organisms capable of acting directly on free nitrogen independent of other plant growth, but the significance of this possible source of plant food is, at the present time, unknown. (5) The micro-organisms of importance to agriculture may be isolated and developed to the exclusion of other organisms of a similar character. This isolation is best accomplished in culture-media consisting essentially of a mineral gelatin to which is added only pure carbohydrates and the necessary mineral nourishment. (6) The nitrifying ferments consist probably of several species, of different geographic distribution. Different types of soil probably have nitrifying organisms of different properties. This is illustrated by the fact that nitrification is accomplished in dry alkaline soils under conditions in which the ordinary nitrifying

organisms would fail to develop. (7) The study of typical soils in respect of the kind, activity, and vigor of their nitrifying organisms has become as important a factor in soil analysis as the usual determination of physical and chemical composition.

DETERMINATION OF NITRIC AND NITROUS ACIDS IN SOILS.

512. Classification of Methods.—The minute quantities in which highly oxidized nitrogen exists in soils render the operations of its quantitative estimation extremely delicate. On the other hand, the easy solubility of these forms of combination and the absence of absorptive powers therefore in the soil, render the separation of them from the soil a matter of great ease. It is possible, therefore, to secure all the nitrates and nitrites present in a large quantity of earth in a solution which can be concentrated under proper precautions to a volume convenient for manipulation. The method of this extraction is the same for all the processes of determination. The methods of analysis suited to soil extracts, as a rule, may also be used in the determination of the same compounds in rain, drainage, and sewage waters, and for the qualitative and quantitative control of the progress of nitrification. The various processes employed may be classified as follows:

1. The conversion of the nitrogen into the gaseous state and the determination of its volume directly. This is accomplished by combustion with copper oxid and metallic copper.

2. The conversion of the nitrogen into nitric oxid and the volumetric determination thereof. The decomposition of a nitrate with ferrous chlorid in the presence of free hydrochloric acid is an instance of this type of methods.

3. The oxidation of colored organic solutions and the consequent disappearance of the characteristic color, or its change into a different tint. The indigo and indigotin processes are examples of this method.

4. The production of color, in a colorless or practically colorless solution, by the treatment thereof with the nitrate in presence of an acid which decomposes it with the liberation of oxidizing compounds. The depth of color produced is compared with that formed by a known quantity of a pure nitrate solution until the

two colorations are alike. The methods depending on the use of carbazol or acid phenol sulfate illustrate this class of reactions.

5. The conversion of the nitrogen into ammonia by moist combustion with sulfuric acid in the presence of certain organic compounds, *e.g.*, salicylic acid, and the collection of the ammonia in standard acid, the excess of which is determined by titration.

6. The reduction of nitrates to ammonia by nascent hydrogen and the recovery of the ammonia produced by distillation and collection in standard acid.

7. The reduction of nitrates by electrolytic action and the collection of the ammonia as above.

8. The decomposition of nitrates with the quantitative evolution of a different element, and the direct or indirect measurement of the evolved substance. The quantitative evolution of chlorine on treating a nitrate with hydrochloric acid, the collection of the chlorine in potassium iodide, and the determination of the iodine set free, form a process belonging here.

513. Relative Merit of Methods.—The process mentioned in the classifications embraced under numbers (1) and (5) of the preceding schedule are sufficiently described in the paragraphs devoted thereto, under soil and fertilizers. In practice at the present time it is rare to determine the nitrogen in nitrates by the copper oxide method. The more rapid if not equally scientific processes of colorimetric comparison or reduction by nascent hydrogen are to be preferred when only small quantities are present.

The indigo methods among the colorimetric processes are not so much in use now as those which depend on the development of a color. Lawes and Gilbert considered them far inferior to the Schloësing method. The developed color methods are especially delicate and are to be preferred in all cases where the detection of the merest traces of nitrates is desired. Where nitrates are present in considerable quantities the reduction method with nascent hydrogen is to be preferred over all others. In all these cases the judgment of the analyst must be exercised. The particular method to be employed in any given case can not be determined save by the intelligent discrimination of the operator. Since these methods are also applicable to the determination of oxidized

nitrogen in fertilizers the detailed discussion of them will be given in volume second. Those peculiarly suited to determine the traces of nitrous and nitric acid in the small quantities produced in nitrification studies are given in previous paragraphs 474 and 475.

514. The Extraction of Nitric Acid from the Soil.—The easy solubility of nitric acid and of nitrates in water is taken advantage of in the separation of these bodies from the soil. A convenient quantity, usually about 1,000 grams of the fine soil, is used for the extraction. Instead of freeing the soil entirely from water, it is better to determine the amount of water in the air-dried or prepared sample, and base the calculation on 1,000 grams of the water-free soil.

All samples of soil for the purpose of examining for nitrates, should be rapidly dried to prevent the process of nitrification from continuing after the sample is secured. For this purpose the soil should be placed in a thin layer in a warm place, 50°-60°, until air-dried. It still contains in this case a little moisture but not enough to permit nitrification to go on.

One thousand grams of soil prepared as above are treated with 2,000 cubic centimeters of distilled water, free of nitric acid, and allowed to stand for 48 hours with frequent shaking. One thousand cubic centimeters of the extract are then filtered, corresponding to 500 grams of the dry soil. A small quantity of pure sodium carbonate should be added to the filtrate which is then evaporated on a water-bath to a volume of about 100 cubic centimeters. Should a precipitate be formed during evaporation it should be separated by filtration, the filter washed thoroughly, and the filtrate again evaporated to a volume of 100 cubic centimeters.

For the determination of nitrates, it is well to extend the sampling to a considerable depth. If the sampling extend only to the depth of nine inches, it should be in dry weather when the nitrates are near the surface.

The temperature at which a soil is dried has also an influence on the quality of nitric nitrogen remaining after desiccation.

If a wet soil be dried at 100°, the nitrates present will suffer partial decomposition. This is probably due to deoxidation by organic matter present. On the other hand, ordinary air-drying

affords opportunity for continued nitrification, thus increasing the residuum of oxidized nitrogen.

The method of drying practiced at Rothamsted, in order to secure results as nearly accurate as possible is the following:⁷³

The soil is broken up directly after it is taken from the field, and spread on trays in layers one inch deep. The trays are then placed in a room at 55°. The drying is completed in 24 hours. After drying, stones and roots are removed, and the soil is finely powdered and placed in bottles.

For extracting the nitrates, a funnel is prepared by cutting off the bottom from a bottle four and a half inches in diameter. A nicely fitting disk of copper gauze is placed in the bottom of this funnel, and this is covered with two filter papers, the upper one having a slightly greater diameter than the lower. The paper is first moistened, and then from 200 to 500 grams of the dry powdered soil introduced. The funnel is connected with the receiving flask of a filter pump, and pure water poured on the soil until it is thoroughly saturated. The water is then added in small quantities. When the filtrate amounts to 100 cubic centimeters the process may be discontinued, since all the nitrates in the soil will be found in this part of the filtrate.

The extract obtained as above is evaporated to convenient bulk for the determination of nitric nitrogen.

⁷³ *Journal of the Chemical Society (Trans.)*, 1882, **41** : 357.

PART EIGHTH

SPECIAL EXAMINATION OF WATERS, VEGETABLE SOILS, AND UNUSUAL SOIL CONSTITUENTS.

515. Further Examination of Waters.—Having described in the preceding part methods of determining the oxidized nitrogen in the products of nitrification where the quantity is very minute, there remains to be considered the examination of waters and soil extracts for other substances of importance to agriculture. Rain waters add practically nothing to the soil of value as a plant food but nitric acid and ammonia, and, therefore, demand no further discussion here. In drainage and sewage waters, in addition to the oxidized nitrogen, there may be sufficient quantities of phosphoric acid and potash to make their further analysis of interest. But by far the most practical point to be considered is in the case of waters used for irrigation purposes where the continued addition to the soil of mineral matters may eventually convert fertile fields into barren wastes. In irrigated lands where there is practically no drainage nearly the whole of the water is removed by superficial evaporation. It is easily seen in such a case how these mineral matters tend to accumulate in that part of the soil in which the rootlets of plants seek their nourishment.

516. Sampling Waters for Irrigation.—To secure a sample of irrigation water from a reservoir, which will represent the entire body of water, is a comparatively easy matter. The method followed in the Bureau of Chemistry is as follows: It is only necessary to get small and equal sub-samples from just below the surface, about half way down, and about two feet from the bottom of the reservoir, at several different points, and mix all the sub-samples thus obtained.

In the case of irrigation waters from streams the following procedure is followed in securing a sample which will represent the stream at any particular time:

Small and equal sub-samples are obtained at the surface half way down, and about two feet from the bottom, at a number of points equidistant from each other and transverse to the stream.

All of the samples are mixed and an aliquot part represents the daily sample.

If the true value of a stream for irrigation purposes is desired, even this single sample is valueless. The only method of attacking such a question as this is to mix equal daily samples secured as above in weekly periods and subject the weekly samples to a chemical examination. Even this method is applicable only so long as the stream has a fairly constant flow. In floods periods or when the character of the water evidently changes materially, a new composite should be started, and sampling continued daily as long as the flood continues. If this flood period extends over more than one week, more than one composite is necessary.

517. Estimation of Total Solid Matter.—The total solid contents of a sample of water are determined by evaporating a known quantity to dryness and weighing the residue. For comparative purposes a given volume of water, measured at a temperature of about $15^{\circ}.5$, may be used if the solid contents do not exceed four grams in a United States gallon, and each cubic centimeter then represents a weight of one gram. Where the content of mineral matter is greater it is best to weigh the water and calculate the solid contents to parts per one hundred thousand or million. Formerly it was customary in the United States to state the content of solid matter in grains per gallon. Since, however, the gallon has so many different values it is always necessary to indicate what particular measure is meant.

In ordinary spring and well waters a convenient volume is 100 cubic centimeters. To avoid calculation a volume in cubic centimeters corresponding to some decimal part of a gallon in grains is employed and the weight in milligrams will then be equivalent to grains per gallon. Thus in the imperial gallon which contains 70,000 grains of distilled water at $15^{\circ}.5$ if the residue after evaporating 70 cubic centimeters weigh 25 milligrams the water contains 25 grains of solid matter per gallon. The United States gallon at $15^{\circ}.5$ contains 58,304 grains of distilled water. In this case 58.3 cubic centimeters should be used, or double this amount and the weight in milligrams be divided by two.

The evaporation may be made in a platinum, porcelain, or

aluminum dish, preferably with a flat bottom. The dish does not need to hold the whole volume at once, but the water may be added from time to time as the evaporation continues. The dish, however, should, as a rule, hold not less than 100 cubic centimeters. The evaporation is best conducted over a steam-bath, and after the complete disappearance of the liquid the heating should be continued until the residue is perfectly dry.

In the case of mineral waters highly impregnated with inorganic salts, a smaller volume or weight is advisable, and greater care must be exercised in drying the residue. For the purpose of determining the percentages of special ingredients, quantities of the water inversely corresponding to the content of the ingredients desired are used. In general, for this purpose, it will not be necessary to evaporate the sample to complete dryness, but only to concentrate it to a volume convenient for the application of the analytical process. Where a complete quantitative analysis of the solid residue is desired, a sufficient quantity of the water is evaporated to give a weighable amount of the least abundant ingredients. The total solid content of the water having been previously determined, the actual weight or volume of the water evaporated to obtain the above residue is of no importance in so far as calculations are concerned.

518. Estimation of the Chlorin.—The chlorin in the solid residue from a sample of water may be determined directly by dissolving the soluble salts in distilled water, to which enough nitric acid is added to keep the solution slightly acid. After filtering and washing, silver nitrate is added, little by little, with constant shaking until a further addition of the reagent produces no further precipitate. The beaker or flask is placed in a dark place, on a shaking apparatus which is kept in motion until the precipitate has entirely settled in a granular state. The silver chlorid is collected on a gooch, washed free of all soluble matter, dried at 150°, and weighed. If the precipitate be ignited to incipient fusion, a porcelain gooch should be used.

A more convenient method is to determine the chlorin directly in the water, or, where the quantity is too minute, after proper concentration, volumetrically by means of a titrated solution of silver nitrate, using potassium chromate as indicator. As soon as

the chlorin has all united with the silver, any additional quantity of the silver nitrate will form red silver chromate, the permanent appearance of which indicates the end of the reaction. This process is especially applicable to water, which in a neutral state contains no other acids capable of precipitating silver. The chromate indicator is not applicable in an acid solution.

519. Solutions Employed.—A quantity of pure silver nitrate, about five grams, is dissolved in pure water and made up to a volume of one liter. For determining the actual strength of the solution, 0.824 gram of pure sodium chlorid is dissolved in water and the volume made up to half a liter. Twenty-five cubic centimeters of this solution are placed in a porcelain dish, and a few drops of the solution of potassium chromate added. The silver nitrate solution is allowed to flow into the porcelain dish from a burette graduated to tenths of a cubic centimeter. The red color produced as each drop falls, disappears on stirring as long as there is any undecomposed chlorid. Finally a point is reached when the red color becomes permanent, a single drop in excess of the silver nitrate being sufficient to impart a faint red tint to the contents of the dish.

The solution of pure potassium chromate is prepared by dissolving five grams of the salt in 100 cubic centimeters of water. Water with any considerable quantity of chlorin can be treated directly with the reagents, but when the percentage of chlorin is low, previous concentration to a convenient volume is advisable.

In waters containing bromids and iodids these halogens would be included with the chlorin estimated as above. For agricultural purposes such waters have little importance. In the case of soluble carbonates capable of precipitating silver this action can be prevented by acidifying the water with nitric acid and afterwards removing the excess of acid with precipitated calcium carbonate. In this reaction McElroy recommends the use of Congo paper, which is not affected by the carbon dioxid but is turned blue as soon as an excess of nitric acid is added. After the addition of the calcium carbonate the mixture should be boiled to expel carbon dioxid.¹⁴

¹⁴ Bulletin No. 13, Division of Chemistry, Part 8 : 1021.

Irrigation waters from ordinary sources or derived from sewage rarely contain enough chlorin to make their use objectionable. On the other hand, when water is obtained for this purpose from near the sea or from artesian wells or from some rivers or streams, especially in time of drought, it may often contain a quantity of chlorin which will eventually do more harm to the arable soil than the water will do good.

520. Carbon Dioxid.—Free carbon dioxid in water has no significance in respect of its use for irrigation purposes. Such waters, however, are usually of a highly mineral nature and thus are justly open to suspicion when used for farm animals and on the field. The presence of free carbon dioxid as has already been pointed out in paragraph 42, gives to water, one of its chief sources of power as an agent for dissolving rocks and ultimately forming soil. The estimation of the total free carbon dioxid in a sample of water issuing from a spring or well is a matter of some delicacy by reason of the tendency of this gas to escape as soon as the water reaches the open air, and is relieved from the natural pressure to which it has been subjected. The actual quantity at the time of exit from the earth can only be determined on the spot and with many precautions. The actual quantity of the gas remaining in solution at any given time is determined as follows: One hundred cubic centimeters of the water are placed in a flask with three cubic centimeters of a saturated solution of calcium and two of ammonium chlorid. To this mixture are added 45 cubic centimeters of a titrated solution of calcium hydroxid. The flask is stoppered, well-shaken, and set aside for 12 hours to allow the complete separation of the calcium carbonate formed.

When the supernatant liquid is perfectly clear an aliquot part thereof, from 50 to 100 cubic centimeters, is removed, and titrated with decinormal acid, using phenacetin or lacmoid as an indicator. From the quantity of calcium hydroxid remaining unprecipitated the amount which has been converted into carbonate is calculated. The weight of carbon dioxid fixed as carbonate is determined by multiplying the number representing the weight of uncombined calcium hydroxid by 0.0022.

521. Examination of Irrigation Waters.—In the method follow-

ed by Haywood in the Bureau of Chemistry for examining irrigation waters the constituents usually determined are: the sulfuric acid ion, the carbonic and bicarbonic acid ions, chlorin, iron, aluminum, calcium, magnesium, sodium and black alkali, and sometimes silica, potassium and the nitric acid ion.

The acid and basic ions are determined by the methods in ordinary use, except that the combined sodium and potassium are weighed as sulfates instead of chlorids and the potash is then determined by the Lindo-Gladding method, described in volume second.

Black Alkali.—Black alkali is determined as follows:

The solutions required are:

Standard sodium carbonate $\frac{1}{25}$ normal.

Standard sulfuric acid $\frac{1}{25}$ normal.

Chloroform.

Erythrosin indicator:—0.25 grams of erythrosin dissolved in one liter of water.

Manipulation.—Two hundred cubic centimeters of water are placed in a platinum or silver dish and 50 cubic centimeters of the $\frac{N}{25}$ sodium carbonate added. The contents of the dish are evaporated on the water- or steam-bath to complete dryness. The residue is rubbed up with distilled water free from CO_2 and transferred to a 100 cubic centimeter flask, made up to the mark, thoroughly shaken, and allowed to stand until the insoluble matter has completely settled. Fifty cubic centimeters of the clear supernatant liquid are transferred to a glass stoppered bottle of 200 or 250 cubic centimeters capacity. The bottle should be of the best white glass. Five cubic centimeters of chloroform and one cubic centimeter of the erythrosin are added and the solution titrated with $\frac{N}{25}$ sulfuric acid. The 50 cubic centimeters aliquot represents 100 cubic centimeters of the original sample of water + 25 cubic centimeters $\frac{N}{25}$ sodium carbonate. If less sulfuric acid is required for this titration than is necessary to balance the sodium carbonate added, part of the sodium carbonate has been used up by a reaction between some of the soluble salts of lime or magnesia and the sodium carbonate; *e. g.*, $\text{CaSO}_4 + \text{Na}_2\text{CO}_3 = \text{CaCO}_3 + \text{Na}_2\text{SO}_4$, in which case the water is said to be hard, and the hard-

ness expressed in terms of calcium sulfate or calcium carbonate, preferably the former. But if more than the equivalent amount of sulfuric acid is required than is necessary to balance the sodium carbonate added, then the sample is shown to have originally contained an excess of alkalinity, which it is customary to express in terms of sodium carbonate or "black alkali."

522. Determination of Carbonates and Bicarbonates.—The method used by Haywood in the water laboratory of the Bureau of Chemistry is the same as that of Cameron,¹⁵ with a few added precautionary details. The following solutions are needed for the work:

- (1) A $N/_{20}$ solution of potassium acid sulfate.
- (2) Methyl orange and phenolphthalein solutions.

The method is as follows:

To 100 cubic centimeters of the water are added a few drops of phenolphthalein. When carbonates are present the usual red color will be evident. The solution is now treated with a $N/_{20}$ solution of potassium acid sulfate, adding the $KHSO_4$ at the rate of a drop every few seconds until the red color has completely disappeared. Towards the end of the reaction when the pink color becomes faint, the solution is stirred vigorously and a couple of drops of the $KHSO_4$ solution only added every minute. The reading on the burette is recorded and represents the conversion of carbonates into bicarbonates. One drop (not more) of methyl orange is now added which produces a pure yellow color. The titration with $KHSO_4$ solution is continued without refilling the burette until the faintest pink blush can be noted in the yellow solution. This is taken as the second end-point and the reading is made.

The first reading gives the amount of $N/_{20}$ $KHSO_4$ necessary to convert carbonates to bicarbonates and must be multiplied by .002979 to get the CO_3 ions present.

The second reading gives the number of cubic centimeters of $N/_{20}$ $KHSO_4$ necessary to convert the carbonates to bicarbonates plus the number of cubic centimeters necessary to act on the bi-

¹⁵ American Chemical Journal, 1900, 23 : 471; 1906, 28 : 77.

carbonates formed in this reaction plus the number of cubic centimeters necessary to act on the bicarbonates already present in the solution. The number of cubic centimeters necessary to act on the bicarbonates already present is therefore found by subtracting twice the first reading from the total second reading. This multiplied by .003028 gives the grams of HCO_3 ions present.

Methods of Stating Results.—The results of analysis are stated in terms of parts per million of the various basic and acid ions present with the exception of silica, which is reported as such.

In combining the ions to form salts, the following procedure is used. If the "black alkali" figure is positive it is reported as sodium carbonate, if negative it is reported as calcium sulfate or calcium carbonate. The amounts of acid and basic ions corresponding to the black alkali are then subtracted from the total amounts of these constituents as found in the complete analysis. The residual basic and acid ions are then combined with each other in the following order: Ca, Mg, K, Na, to carbonic acid, bicarbonic acid, sulfuric acid and chlorin ions. Silica is reported as such and iron and alumina as the oxids.

523. Other Constituents.—The lime, magnesia, iron, alumina, potash, soda, sulfuric acid, nitric acid, chlorin, etc., are determined in the evaporated residue of large quantities of water by the methods in common use. In brackish water or mineral waters containing large quantities of common salt the chlorin may be estimated in solution without concentration.

524. Extraction of Soil Water Unchanged.—It is desirable to have a just conception of the composition of the aqueous content of the soil in a condition as nearly as possible that in which it actually exists. Schlösing has devised the following method of securing such a sample.⁷⁶ Soil which has just been taken from a field is placed in a powdered condition in a vertical cylinder and sprinkled lightly with an artificial rain of pure water. Divide the cylinder into very thin horizontal layers and suppose that the rain descends by parallel surfaces. The upper layer saturated with water yields to the next lower layer a first mixture of water and of solutions contained in the soil. The second will yield to the third a

⁷⁶ Comptes rendus, 1866, 63 : 1007.

mixture slightly richer and thus in regular order until a given layer will receive from the preceding one a solution of which the composition will be infinitely near that of the solution pre-existent. Beginning with this layer the portion of the solution contained in the layers lying under will be simply replaced and thrust finally without the containing vessel. Received by itself it becomes a sample representing in composition the moisture originally present in the soil.

A proof of the correctness of the theory is as follows: 1.2 kilograms of sand, washed and dried, was moistened with 200 cubic centimeters of a solution of common salt containing ten milligrams of chlorin per cubic centimeter. This was introduced into a vessel similar to the one described, covered with a roll of moist cotton for the purpose of distributing equally the pure water which was added at the rate of 40 cubic centimeters per hour. The liquid which was driven out was received in quantities of ten cubic centimeters. Each three quantities were placed together and the chlorin determined therefrom. The first three quantities contained 100.2 per cent, the second three 99.8 per cent, the third three 99.8 per cent, the fourth three 100 per cent, the fifth three 100 per cent, and from this point the quantity of chlorin rapidly diminished. The tenth three portions contained none. Thus it is seen that three-fourths, at least, of the solution in the sand was displaced without mixture with the added water. Other determinations were made to show that the solution which would be forced from a soil in a similar manner must correspond to that preexistent therein. In this way the normal and natural solutions in soils can be obtained in large quantities.

Applying the method to soils in a series of experimental research Schlösing reached the following conclusions: The first products received have a constant composition; these experiments bring into evidence effects to which little attention has been given, namely, the proportion of fertilizing principles carried off by the rain into the subsoil depends not only upon the quantity of water which falls, but also upon the state of humidity of the soil before the rain. For example, after a drought quantities of rain sufficient to saturate the soil and make infiltrations beyond the use-

ful portion of the soil will be able to cause more loss than a rain much less intense falling upon a soil already humid. Indeed, when there is placed in the presence of equal weights of soil solution, alkali solutions identical in composition but unequal in volume, the lot of soil placed in the presence of the largest volume will absorb much of the alkali; but when the solutions are displaced by water, solutions of alkaline salts are accumulated in the inferior layers. Although the alkaline solutions were at first impoverished by the absorption power of the soils, this did not prevent the establishment of a new equilibrium from which results the constancy of the composition of the first liquid received.

Chevreul,⁷⁷ in discussing this theory, calls the attention of the Academy to the communication which he made on the 6th of June, 1853, recognizing the effect which a solid body insoluble in a liquid holding another body in solution is capable of producing upon that solution and that the method had pointed out three possible cases; first, where the solid matter takes more of the solvent than of the bodies dissolved; there is in that case a concentration of the solution. Second, the contrary case; third, finally the mean case where the solution after contact preserves its original state. The following experiments were made in connection with this: (1) Upon lime water placed in contact with glass, with sand, etc.; (2) Upon cotton, silk, and wool placed in contact with chlorid of sodium, with bichlorid of mercury, sulfuric acid, etc.

From the above it is seen that some of the general principles of physical chemistry were well recognized by Chevreul more than fifty years ago.

This method of displacing and obtaining the water content in the soils is well suited to the study of dissolved bodies in their natural state and has not received the attention its merits warrant. It permits operations to be carried on in the laboratory and under the most varied circumstances. Since its first publication Schlösing has sensibly improved it.⁷⁸ The displacement is secured from 30 to 35 kilograms of powdered soil in a large bell-jar as soon as possible after it is taken from the field. The artificial rain de-

⁷⁷ *Comptes rendus*, 1856, **63** : 1012.

⁷⁸ *Comptes rendus*, 1870, **70** : 98.

signed to replace the solution is distributed by a mechanism driven by a little hydraulic motor, which distributes the rain as gently as one could wish, for example, a half liter in 24 hours, and with such uniformity that the line of demarcation between the color of the earth saturated with water and that of the earth simply humid is maintained constantly in a horizontal plane during its descent, which may last three, four, or even eight days. The dispositions thus adopted permit of the analysis of the air confined in the earth, of the circulation therein of pure air or air charged with a given content of carbonic acid, and further permit the liquids to be received out of contact with the air in the laboratory and in an atmosphere the same as that of the original earth, a precaution which avoids the loss of carbonic acid and the consequent deposition of matters which this gas holds in solution.

Estimation of Carbon Dioxid.—The determination of the carbonic acid in the waters of the soil by this process is made twice by boiling. The first ebullition gives that which is free or combined as bicarbonates; the second ebullition after the addition of an acid gives that combined as neutral carbonates. Schlösing has shown that in a boiling liquor the dissolved silicic acid partially decomposes the carbonates of lime and of magnesia, from which it is inevitably certain that the first operation gives an excess of gas if it is too prolonged, or a loss if it is not prolonged enough. It is not surprising, therefore, if in such analyses there is not an absolute equality between the sum of the equivalents of the bases and that of the equivalents of the acids.

Quantities of Phosphoric Acid.—Further information concerning the composition of the solutions obtained from the soil gives the total phosphoric acid in conjunction with the iron, the largest amount of the two together in any one soil was 2.8 parts per million. Five of the samples contained no phosphoric acid and iron in the solutions. Only three out of the 18 samples had above one part per million.

It is thus seen that in the soil moisture which must be absolutely normal, the quantities of phosphoric acid even when augmented by the iron present are found to be extremely minute.

525. Quantity of Phosphoric Acid in Soil Water.—It is known

that the water existing in soil holds in solution a very small quantity of phosphoric acid. This quantity is embraced usually between a few hundredths of a milligram to one milligram per liter, some times reaching as much as two or three milligrams, and in the opinion of some authorities appears generally without importance for the nutrition of plants.⁷⁹ In fact, a hectare, comprising 3,000 tons of earth, having 15 per cent of water and one milligram of phosphoric acid per liter in this water, would contain in the dissolved state only .45 kilogram of phosphoric acid, a quantity relatively very small to the content of the crop.

It has also been generally admitted, since the classical experiments of Sachs and others, that the essential source of phosphorus for vegetables resides in the phosphates not dissolved in the soil, phosphates attacked by the acid juices of the roots and utilized strains too much the rôle of the phosphoric acid which is found in the waters of the soil in a state of solution. This question has already been examined by Joffe in regard to the action of superphosphates.⁸⁰ The process employed in the extraction of the soil water is founded on the process which displaces the soil water very slowly by water poured in a regular shower over the surface of the soil.⁸¹ If 40 kilograms of soil are treated in this way under proper conditions this process furnishes generally at least one liter of the same solution as that which existed in the soil without sensible alteration.

In the solution thus obtained Schlösing determines the phosphoric acid according to the method outlined below. The method consists in the evaporation in a flask of one liter of the soil water, to which is added a little nitric acid to drive off any hydrochloric acid present. The process is finished by evaporating to dryness in a platinum capsule and incinerating to destroy organic matter. After the addition of a small quantity of nitrate of ammonia the capsule is heated to render the silica insoluble, taken up with acidulated water and filtered. In the filtered liquor reduced to a very small

⁷⁹ *Comptes rendus*, 1898, 127 : 236.

⁸⁰ *Bulletin de la Société chimique, de Paris*, 1895-98, [3], 13 : 698.

⁸¹ Schlösing père, *Comptes rendus*, 1870, 70 : 98.

volume, (from two to four cubic centimeters), phosphoric acid is precipitated by molybdate of ammonia and determined with the usual precautions. In ordinary cases the quantity of lime is not in sufficient proportion to interfere with the determination, but frequently solutions are encountered in which it is desirable to eliminate the sulfuric acid with a view of avoiding an excess of sulfate of lime. The determinations by means of the phospho-molybdate reagent can be made with great precision. In seven different soils in which 40 kilograms of each were treated according to the above method the quantities of phosphoric acid per million were as follows: 1.02, 1.19, 1.05, 1.04, .98, .09, and .12, respectively.

The phosphoric acid which is dissolved in a soil results from the equilibrium between chemical actions which are very complex, tending on the one hand to render the phosphoric acid insoluble, and on the other hand to make it pass into solution in such a way that if by some cause the proportion of phosphoric acid dissolved diminishes, a new quantity of acid enters into solution in order to establish the primitive quantity, and *vice versa*. By the play of the phenomena of equilibrium, the phosphoric acid is capable of renewing itself in the waters of the soil in proportion as the vegetation consumes it. Whence, in spite of its feeble proportion, it is no longer to be deemed altogether negligible for the alimentation of plants.

526. Quantity of Phosphoric Acid Necessary to Plant Growth.—

It has been generally thought that the phosphoric acid contained in the solutions impregnating the soil cannot, on account of its being always present in minute proportion, be of any very great utility and is almost negligible for vegetation. The younger Schlösing, on the contrary, has been led to think that, in spite of its rarity, it should be taken into serious consideration as a source of phosphorus for plants.⁸² This rarity, indeed, is only in appearance, because phosphoric acid is able to renew itself in the solutions of the soil in proportion as the roots cause it to disappear. This renewal results in an equilibrium which without cessation tends to be established between the water and the almost in-

⁸² *Comptes rendus*, 1898, 127 : 820.

finitely little soluble phosphates of the soil. This equilibrium is established also with a tolerably great activity in a soil which is gently shaken with water. It is accomplished, as has been shown, in a few hours, in such a way that during the course of a season of vegetation it is capable of furnishing to plants a good part of the phosphoric acid which they absorb.

It might be useful to push the demonstration further and to prove not only that the solutions of the soil can offer to plants an important quantity of phosphoric acid, but also that the plants can really secure their food exclusively or in a major part from the phosphoric acid present in a state of solution and in the very small doses which are met with in the waters of the soil.

Although many experiments have been made on the utilization of phosphoric acid by plants it does not appear that one has been made under the conditions in which by a gradual reduction of the phosphoric acid supplied in the water the limit of growth and development was determined. To ascertain this point, maize, beans, and wheat were cultivated on sterile soils, irrigated with nutritive solutions in which the phosphoric acid in a soluble state varied from nothing to two milligrams per liter, that is, two parts per million. These experiments show that when the amount of phosphoric acid reaches two milligrams per liter plants are produced of full growth, while when the amount of phosphoric acid is reduced to less than one-tenth milligram per liter the plants are dwarfed and only slightly developed. When sterile soils unsuited by themselves to properly feed plants with phosphoric acid are irrigated with nutritive liquids containing this acid in different proportions, plants have been able to take phosphoric acid almost exclusively from the solutions of it which was offered them. Without the addition of phosphoric acid in these solutions the plants remained undeveloped. In presence of the solutions containing the quantities of phosphoric acid in the order in which they exist in arable soils they have prospered. With solutions containing two milligrams of phosphoric acid per liter there was obtained a very good crop of maize, and with solutions which contained one-half milligram and one milligram, respectively, the harvests of wheat corresponded to ten and 18 hectoliters per hectare, respectively.

527. Colorimetric Estimation of Phosphoric Acid.—It has been shown that in soil waters only minute traces of phosphoric acid are usually found. Attempts have been made to determine such traces, often too small for gravimetric treatment, colorimetrically. The methods proposed for this purpose have been reviewed by Veitch.⁵³ The methods of Lepiere⁵⁴ and of Woodman and Cayvan⁵⁵ promised the most valuable results.

The chief difficulty in the process is due to the necessity of removing from the solution all matters except phosphoric acid, which affect the color of the solution. Among these silica is the most active, but organic matter, aluminum sulfate and iron have much interfering power. All suspended matter is first removed by filtering through paper or through porcelain and organic matter is then destroyed, which is best accomplished by ignition with magnesium nitrate and subsequent evaporation with nitric acid. Traces of silica in equivalent proportions have about 1.8 times more power to form color with an ammonium molybdate solution than phosphoric acid. Its entire removal is, therefore, a condition of even approximately accurate results. Schreiner⁵⁶ having observed that silica solutions give different intensities of coloration under different conditions, uses this fact as the basis for the estimation of both silica and phosphoric acid without removal of the silica. In the solution are found in a given case silica and phosphoric acid. Under certain conditions silica gives a color reading only half as great as that given under another condition, but phosphates always give the same color. The results are calculated from the following formulæ

$$(1) \quad x + y = a$$

$$(2) \quad \frac{1}{2}x + y = b$$

where x equals silica, y equals phosphoric acid, " a " equals the reading under one condition and " b " equals the reading under the other condition.

Determination of the "a" Reading.—To 50 cubic centimeters of the solution add five cubic centimeters of nitric acid reagent and

⁵³ Journal of the American Chemical Society, 1903, **25** : 169.

⁵⁴ Bulletin Société Chimique de Paris, 1896, [3], **15** : 1213.

⁵⁵ Journal of the American Chemical Society, 1901, **23** : 96.

⁵⁶ Journal of the American Chemical Society, 1902, **24** : 111.

four cubic centimeters of ammonium molybdate reagent, and after 20 minutes the color reading is made.

Determination of the "b" Reading.—To a second portion of 50 cubic centimeters of the solution add four cubic centimeters of ammonium molybdate solution and allow to stand one hour, then add five cubic centimeters of nitric acid reagent making the readings and the values of phosphoric acid and silica readily calculated. The silica reading is twice the difference between the "a" and "b" readings. The silica reading multiplied by .00525 equals milligrams of silica and the phosphoric acid reading multiplied by .01 equals milligrams of P_2O_5 .

The accuracy of the method has been confirmed by Lincoln and Barker.⁸⁷

In pure colorless solutions the colorimetric method as conducted by Veitch gives results fairly concordant with the official gravimetric and volumetric determinations. The attempt to apply colorimetric methods to soil extracts directly may lead to grave errors even in experienced hands and to avoid this all the precautions mentioned should be observed. The use of more concentrated extracts carefully freed of interfering bodies is therefore to be advised and these are conveniently obtained by evaporating a large volume of the extract.

As is well observed by Veitch, the method is so delicate and it has been shown there are so many points at which errors may be introduced that the following precautions must be observed if anything like accuracy is to be reached.

The sodium phosphate ($Na_2HPO_4 + 12H_2O$) from which the standard is made must be practically pure, and be free from silica and iron. It is convenient to make a solution containing 100 parts phosphorus pentoxid per liter, and then dilute this to ten parts per liter for the reading standard. The greatest care should be used in making this standard as it is here where errors count. Ten cubic centimeters of the 100 parts per liter solution should be run into a standardized 100 cubic centimeter flask from an accurately graduated burette. Dilute to about 80 cc. at 20°-25° with distilled water (free from SiO_2 and P_2O_5), add ten cubic centi-

⁸⁷ Journal of the American Chemical Society, 1904, 26 : 975.

meters of nitric acid (1.07) and eight cubic centimeters of ammonium molybdate complete to volume and mix thoroughly. This is the standard with which the unknown solutions are to be compared and it should be made fresh each day.

All reagents including distilled water must be kept in Jena glassware, tested from time to time and made fresh when a mixture of them shows color after standing some time.

As the colorimetric tubes may have a slight color themselves, each should be tested and its reading carefully established. This may be done by filling the tubes with distilled water and reading them with a one part per million standard.

The standard and the unknown solution must contain, in equal volumes, equal amounts of reagents and be at sensibly the same temperature.

The solution must contain less than 20 parts per million of iron.

A correction must be established for each package of filter-paper used. This correction is small, but is not to be neglected.

When the solution contains much lime or magnesia it is best to make two evaporations and filtrations before comparing.

The working errors may only be neglected when at least 200 cubic centimeters are taken for the determination.

REAGENTS FOR THE COLORIMETRIC DETERMINATIONS OF PHOSPHORIC ACID.

(1) *Ammonium Molybdate Solution*.—Fifty grams of the pure salt in one liter of solution.

(2) *Nitric Acid* (sp. gr. 1.07).

(3) *Standard Phosphate Solution*.—0.5045 gram of pure freshly crystallized sodium phosphate, $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$, is dissolved in water, 100 cubic centimeters of nitric acid (sp. gr. 1.07) added, and the whole diluted to one liter. The nitric acid is added to lessen the contamination with silica from the glass. One cubic centimeter = 0.0001 gram P_2O_5 .

(4) *Standard Colorimetric Solution*.—This is prepared by diluting ten cubic centimeters of the above standard phosphate solution to about 80 cubic centimeters and then adding nine cubic centimeters of nitric acid (sp. gr. 1.07), and eight cubic centimeters of ammonium molybdate reagent and making up to 100 cubic

centimeters. After standing 20 minutes it is ready for use. Each cubic centimeter of this colorimetric solution is equal to 0.00001 grams P_2O_5 .

528. Colorimeter for Phosphoric Acid Determination.—The colorimeter shown in the accompanying illustration consists essentially of graduated glass tubes containing the standard and the unknown colorimetric solution, the length of the column of liquid in both tubes being changed by means of two smaller immersion tubes, also of glass.⁸⁸ The immersion tubes (A), which are 26 centimeters in length and about two centimeters in diameter, resemble the narrow Nessler tubes, the bottom being well ground and polished. The upper ends of the tubes are mounted in blocks of wood which fit into grooves on the body of the colorimeter as shown. This permits the ready removal of the tubes from the colorimeter for cleaning when the liquids are changed. The graduated tubes (B) have well ground bottoms and are likewise 26 centimeters in length, but have a diameter of about three centimeters. The scale divisions are two millimeters apart. On the reverse side of the tube there is a 50 cubic centimeter and a 100 cubic centimeter mark for making the solutions up to definite volume. These tubes are supported by a block of wood about midway of the camera and are held in place by brass springs or clamps (C), the tension of which can be regulated to suit the diameter of the tube, so as to allow it to be freely moved up or down by hand and yet be firmly held in position when the setting is made. It will be noticed from the figure that the glass tubes diverge slightly. This has been found of advantage, as it allows the operator to look down the center of both immersion tubes, as well as to bring the upper parts of the tubes, and consequently the images, closer together.

The tubes are illuminated from the reflector (D), which carries a white sheet of cardboard or opal glass, and after passing through the tubes the light is reflected by a mirror (E) in the upper part of the instrument to the eye of the observer at (F). The dimensions of the camera are about 70x32x16 centimeters.

To make the comparison the standard colorimetric solution is

⁸⁸ Journal American Chemical Society, 1905, 27 : 1192.

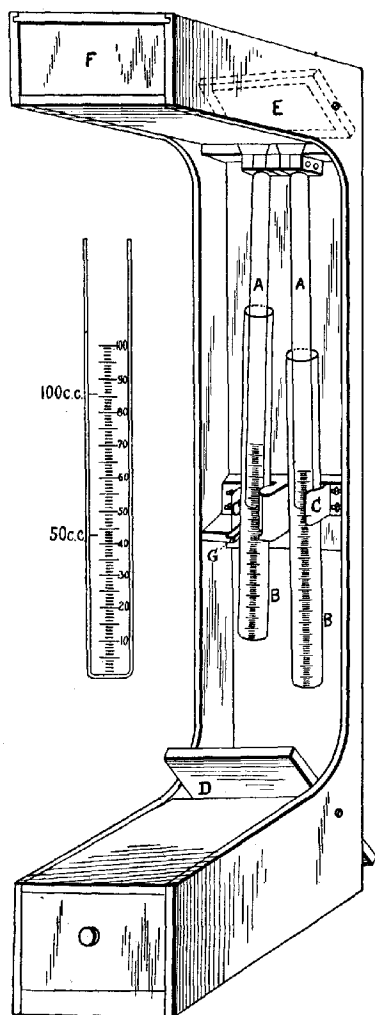


Fig. 90. Colorimeter for Phosphoric Acid Determination.

poured into one of the graduated tubes and put into place with the immersion tube, as shown in the figure. The unknown colorimetric solution, made up to definite volume, is put into the other graduated tube and similarly placed in the instrument. The tube containing the standard is set at a convenient height and the other tube containing the liquid of unknown strength, moved up or down, the operator watching the effect on the images in the mirror through the opening (F). By moving the tube so that the image is alternately weaker or stronger than the standard, the setting can be accurately and quickly made. When both images show the same intensity of color, the setting is read by noting the division mark on the graduated tube opposite the ground bottom of the immersion tube. This reading will give the height of column of the unknown solution which exactly corresponds with the intensity of color of the column of the standard solution. It follows, that the strengths of these two colorimetric solutions are inversely as the heights of the columns; that is, as the readings on the two tubes. If R is the reading of the standard solution of strength S , and r the reading of the colorimetric solution of unknown strengths s , then

$$s = \frac{R}{r} S$$

The same formula, of course, applies when the unknown solution is fixed and the standard moved up or down until the images are of equal intensity. Standard glass slides may be inserted at (G) in place of the tube containing the standard solution. The tube (A) is, however, retained so as to give similar images when viewed from above.

529. Colorimeter of King and Whitson.—Another instrument used prior to the one just described is that of King and Whitson.⁸⁹ It consists of a tube of colorless glass, one inch by ten inches, with a side delivery tube near the bottom to connect by means of a rubber tube with a sliding reservoir for quickly changing the length of the standard colorimetric solution;

⁸⁹ University of Wisconsin Agricultural Experiment Station, Bulletin No. 85 : 38.

a comparison tube, also of colorless glass and as nearly as practicable of the same dimensions as the measuring tube. It is provided with a 50 cubic centimeter and 100 cubic centimeter mark. The measuring tube is graduated so that one division of the scale is exactly equal to 0.01 of the distance between the bottom of the comparison tube and the 100 cubic centimeter mark. Both tubes have accurately ground and polished bottoms. The whole is mounted in a suitably constructed camera. A reflector of white paper, in place of the mirror of the Whitson instrument, at the top of the camera, illuminates the two solutions alike, while the images are viewed in a mirror below.

The water or extract is tested for iron by adding potassium ferrocyanid to the acidified solution. The absence of interfering accounts of iron having been shown, a measured volume of the water or soil extract is freed from suspended matter by filtration or by passing through a porcelain filter (reject the first 100 cubic centimeters that pass) or by evaporating to dryness and filtration, or in some cases where the water is but slightly turbid the turbidity or color is corrected for by determining its amount in terms of the standard, the reading thus obtained being afterwards subtracted from the final readings. Add to the clear extract five cubic centimeters of nitric acid (sp. gr. 1.07) and four cubic centimeters of molybdate solution. Place in the camera, allow 20 minutes for development of color and compare with a standard phosphate solution, which may conveniently contain ten parts per million of phosphorus pentoxid. The color of the standard is not affected by the rubber tube during one working day, but the standard should be made fresh every day. The readings thus obtained (several should be made and the average taken) minus the reading for turbidity, when calculated to a volume of 100 cubic centimeters, equals $P_2O_5 + SiO_2$ in parts per million of solution.

Another measured portion of the water or extract is evaporated to dryness twice (with a filtration between the evaporations) in a porcelain or platinum dish with three cubic centimeters of nitric acid (sp. gr. 1.07) and with a little magnesium nitrate, heated two hours in a water oven, five cubic centimeters of nitric acid

(sp. gr. 1.07) added, filtered, washed to about 45 cubic centimeters, placed in a camera and compared.⁹⁰

If colored, the reading is noted, and is finally subtracted from the total reading. Add four cubic centimeters of ammonium molybdate and thoroughly mix. Place in the camera and compare after five minutes. The corrected reading calculated to a volume of 100 cubic centimeters is P_2O_5 in parts per million of solution. This reading subtracted from the $SiO_2 + P_2O_5$ reading and the difference multiplied by 0.55 gives the silica.

Where lime and magnesia salts are absent a single evaporation to dryness will usually remove all the silica while, in the presence of these salts two or more evaporations are required.

Where the original solution is too much colored with organic matter to be accurately corrected for by reading the color thus produced against the standard phosphate solution, it is necessary to evaporate with about 0.1 gram magnesium nitrate⁹¹ and burn off the organic matter, take up with water to which three cubic centimeters of the nitric acid reagent have been added, evaporate to dryness and heat two hours in the water oven. Add five cubic centimeters of nitric acid and proceed as above. In this case silica is not determined.⁹²

SPECIAL TREATMENT OF PEAT SOILS.

529½. General Considerations.—Deposits of peat which are to be used as soil for cultural purposes, or marsh lands, containing large quantities of organic matter, require a special treatment in addition to the general principles of examination illustrated in the previous pages. These soils, essentially of an organic origin, do not permit of the same treatment either chemical or physical as is practiced with soils of a mineral nature. For instance, it would

⁹⁰ Or the procedure of Schreiner given above may be used.

⁹¹ In solutions containing sufficient base to form normal phosphates with all the phosphoric acid, the addition of magnesium nitrate appears to be unnecessary.

⁹² Or the organic matter may be destroyed by treating with aqua regia in the presence of sufficient base to prevent loss of phosphoric acid.

be useless to attempt a silt analysis with organic soils, and the extraction of them with hydrochloric acid for the purpose of determining the materials passing into solution would prove of little utility. The object of the examination is not only to obtain knowledge of the ultimate constituent of the sample, but also, and this is the practical point, to gain some idea of the stores of plant food in the soil and of the proper steps necessary to secure a supply of the deficient nutrients. The final analytical processes for the estimation of the constituents of a peat or vegetable soil are the same as those already given, but the preliminary treatment is radically different.

530. Sampling.—First of all the geological and meteorological conditions of the peat formations must be determined as nearly as possible. It is fair to presume that these formations are of comparatively recent origin, in fact that they are still in progress of evolution. The geological formation in the vicinity of the deposit should be noted. Information should be obtained in respect to the character of the water, whether running or stagnant, fresh, salt, or brackish, and the changes of level to which it is subject, should be noted. It should be particularly stated whether the vegetable growth contributing to the formation be subject to frost or freezing. The character of the growth is to be carefully noted, and observation made of any changes in vegetation due to drainage preparatory to cultivation. It is to the original vegetation that the chief vegetable accretions in the peat must be accredited. In all cases, for purposes of comparison, some samples must be secured from parts of the field which have not been under cultivation or fertilization. The original properties of the peat can thus be determined and compared with the portions which have been changed under cultivation. If the vegetation in different parts of the field vary it is an indication that the peat is not homogeneous in structure and in such cases all the different kinds must be separately sampled. Any alluvial deposit should be carefully separated from the peat found *in situ*, for the two layers are radically different in nature.

The sampling should be made by digging a pit, if possible to the bottom of the peat formation, and getting the samples at

depths of one foot from one or all of the sides. The samples from sections of even depth are to be mixed and about five kilograms of the well-mixed sample preserved. Blocks of the unbroken and unshattered material should also be taken from each section for the purpose of determining permeability to water and air. All living vegetable matter should be as fully as possible removed before the sampling begins. The nature of the subsoil must be observed, and it should be stated whether it be sand, clay, limestone, etc. Fresh samples should be secured at various depths for the purpose of determining the content of moisture in the manner described in paragraph 75. The tubes used are made sharp at the end to be inserted in the soil, and so arranged as to cut cylinders of soil a trifle smaller than their interior diameter. By this means the sample slips easily into its place. The same care and judgment must be used in securing these samples as are required in the case of common soils.

Illustration.—Samples of peat soil from Runnymede, Florida.

(a) *Formation.*—Littoral fresh-water lacustrine deposits, varying from a few inches to four feet in depth, and from a few feet to half a mile in width.

(b) *Vegetation before drainage.*—Saw grass (*Cladium Mariscus* or *effusum*).

(c) *Principal present vegetation.*—(See pages 49-50).

(d) *Kinds of Soil.*—The peat shows two distinct colors, black and brown. The vegetation, however, seems to be the same in both cases. The black peat has the appearance of being more thoroughly decomposed.

(e) *Geological Formation.*—This portion of the Florida peninsula is covered generally with sand due to marine submergence during recent geological periods. The forest growth is pine. The drainage from the pine land is towards the peat deposits. The pine land lies from four to ten feet higher than the surface of the peat and is much less subject to frost.

531. Water Content.—The capacity of a peat soil for retaining water is very great. In a moist state these soils are heavy and apparently quite firm. When dry they are light and fluffy and unsuited to hold the rootlets of plants. Saturated to their great-

est capacity they hold considerably more than their own weight of water. Attention has already been called to the danger of drying such samples at a high temperature. As in most cases of drying exposure at the temperature of boiling water until a constant weight is obtained is a perfectly safe way. It is hard to say what comes off in addition to water at a higher temperature. All that comes off even at the temperature of boiling water is not water.

The method of determination of water usually employed in the laboratory of the Bureau of Chemistry is the following:

From four to five grams of the material are spread as evenly as possible over the flat bottom of a circular aluminum dish, about seven centimeters in diameter. The dish is exposed for three hours at the temperature of boiling water and then kept for two hours in an air-bath at 110°. At the end of this time constant weight is obtained. Additional drying at 110° for five hours, usually gives no further loss of volatile matter. The dish should be covered during weighing on account of the hygroscopicity of the residue. When well sampled the dry matter thus obtained serves as the basis of calculation for the general analytical data.

Results.—Samples of peat soil placed in brass tubes in March during the dry season had the following contents of moisture:

	Matter volatile at 110° Per cent.
From near the surface.....	61.60
“ one foot below the surface.....	84.35
“ two feet “ “ “	81.52

It is thus seen that the normal content of moisture in such a soil during the dry season, exclusive of the top layer, is about 80 per cent.

The drying of turf, peat or vegetable mold is best conducted in a partial vacuum whereby the action of oxygen on organic matter is excluded. It is well to keep the vessel in which the drying takes place free of all moisture by placing in it a dish of calcium chlorid or phosphoric anhydrid. The desiccator in which the sample is cooled before weighing should contain calcium chlorid or phosphoric anhydrid and not sulfuric acid.⁸⁸

⁸⁸ Landwirtschaftlichen Versuchs-Stationen, 1895, 46 : 221.

532. Organic Carbon and Hydrogen.—The organic carbon and hydrogen in peat soils are determined on the carefully dried sample by combustion with copper oxid. This process gives not only the quantities of these bodies combined as humus, but also those in a less advanced state of decomposition and present as fatty bodies or resins. The method employed is given on pages 345 and following.

Results.—The data obtained on a sample of peat soil from Florida are as follows:

	Per cent. carbon	Per cent. hydrogen
One foot from surface.....	57.67	4.48
Two feet " "	47.07	5.15
Three " " "	8.52	0.53

The last sample was largely mixed with sand, the peat at the point where it was obtained not being quite three feet deep.

533. Total Volatile and Organic Matter and Ash.—The ignition of the sample should be very carefully conducted at the lowest possible temperature. About five grams of the air-dried sample or double that amount of the moist sample will be found to be convenient amounts. In the latter case the calculations should be made on the basis of the dry material. The ignition is continued with frequent stirring with a platinum wire until all organic matter is destroyed. At the same time in a large dish one or more kilograms of the sample is ignited in order to secure an ash for analysis. The ash is quickly weighed to avoid absorption of moisture.

534. Sulfur as Pyrite.—The sulfur present in peat is usually combined either in an organic form or with iron. It may be estimated by the method of Fleischer.⁹⁴

An aqueous extract is made of the sample to be tested and examined for the presence of ferrous oxid by adding a solution of red ferricyanate of potash (Blutlaugensalz) thereto. The presence of iron in the ferrous state is revealed by the blue color produced. Any acid reaction is detected by means of litmus. In the aqueous extract of 100 grams of the peat, potash, soda, lime, magnesia, ferrous and ferric iron, chlorin and sulfuric acid are determined

⁹⁴ Wahnschaffe, *Anleitung zur Wissenschaftlichen Bodenuntersuchung*, 1093, 2nd edition, 147.

and the probable state of combination calculated. Any excess of sulfuric acid is regarded as having been present in a free state.

Twenty grams of the extracted and dried sample are ignited in a hard glass tube in a stream of air or better of oxygen. The sulfur existing as pyrites is converted into sulfuric or sulfurous acid.

The combustion is carried on in the apparatus shown in Fig. 91.

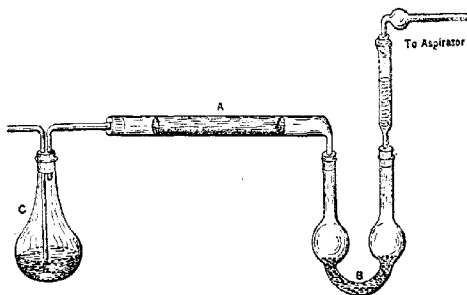


Fig. 91. Apparatus for Determining Sulfur.

The end of the tube A, next to B, is lightly stopped with a plug of glass wool, the substance introduced and held in place by a second plug of glass wool next to C. A is connected to the flask C, containing water, as is shown in the illustration. The chief object of the flask is to control the rate of aspiration of the air or oxygen. A is also connected with the bulb-tube B, as shown in the figure. B contains potash lye, free of sulfur. On the arm of B leading to the aspirator is placed a drying tube filled with glass pearls, moistened with potash lye. This is connected with the aspirator by a small bulb-tube bent at right angles, as indicated. The bulb of this tube contains a little neutral litmus solution, which must suffer no change of color during the progress of the analysis.

The tube, thus arranged, is placed in a combustion furnace and gradually heated to redness, beginning with the part next to B. A moderate stream of air or oxygen is passed through the tube by aspiration during the operation. Any product of the combustion collecting in the tube before reaching B, is driven into B by

careful heating. At the end of the combustion the contents of B are acidified with hydrochloric acid, and treated with bromin to convert the sulfurous into sulfuric acid. The excess of bromin is afterwards removed by boiling, and the sulfuric acid precipitated by barium chlorid and estimated in the usual way.

The total sulfuric acid is not all obtained by this method, but it appears to have some advantages in the examination of peat for sulfur injurious to vegetation.

The sulfuric acid in a peat which is injurious to vegetation is classified by Fleischer, as follows:

(1) Free sulfuric acid, which is the excess obtained after calculation as sulfates of the bases in the water extract before combustion.

(2) The sulfuric acid contained as copperas, calculated from the ferrous oxid content of the aqueous extract.

(3) Sulfuric acid arising from the oxidation of pyrites calculated from the sulfuric acid obtained by combustion of the water-extracted sample. It will be noticed that no account is taken here of the sulfurous acid that might be due to organic sulfur in the peat.

A better idea of the distribution of the sulfur in the sample can be obtained by estimating it according to the method given in paragraph 429.

535. Phosphoric Acid.—A method for determining the phosphorus in peat is given in the next paragraph. The process given in 421 may also be used.

The method of extraction with hydrochloric acid is wholly unreliable as a means of determining the available phosphoric acid in peat.

There are some vegetable soils which contain so much iron and lime that the whole of the acid ordinarily used would be consumed thereby. In some cases it may be found useful to determine the quantity of phosphoric acid which can be extracted with dilute hydrochloric acid, and afterwards to separate the humus and determine the content of phosphoric acid therein.

536. Estimation of Phosphoric Acid in Peat Soils.—The amount of phosphoric acid obtained by extraction with hydrochloric or

sulfuric acid is markedly less in these soils than that obtained after the incineration of the sample, as pointed out by Schmöger.⁹⁸ This is due to the fact that the phosphoric acid is ordinarily combined in the form of nuclein. Extraction of the soils with ether shows that it is not present in the form of lecithin. The nuclein products, as is well known, are decomposed by heating in presence of acidified water at a high temperature for some time. The heating can either take place in an autoclave or in sealed glass tubes. The method is as follows:

The sample of soil is thoroughly rubbed up in a mortar with water, and then hydrochloric acid added until one gram of the water-free peat is suspended in about ten cubic centimeters of 12 per cent hydrochloric acid. The sample is placed in a glass or porcelain vessel in an autoclave and heated to 140°-160° for 12 hours. The phosphoric acid is determined in the extract in the usual way. The percentage of phosphoric acid determined in this way is found to correspond to the amount determined by the incineration of the substance.

The total phosphoric acid is determined in peats by the incineration of the sample and the estimation of the phosphoric acid in the ash. The phosphoric acid soluble in hydrochloric acid solution is determined by extracting a sample of the soil with 12 per cent hydrochloric acid in the usual way. The difference between this and the total is calculated as phosphoric acid in organic compounds.

Or the total phosphoric acid is determined by treating the soil with 12 per cent hydrochloric acid, in the proportion of one gram of soil to ten cubic centimeters of the acid, and the solution is placed in an autoclave and heated for ten hours to 140°-160°, as above described. The phosphoric acid is then determined by the usual method. The difference between the total phosphoric acid as thus determined and the phosphoric acid soluble in hydrochloric acid is calculated as phosphoric acid in organic compounds.

537. Humus.—The humus is estimated by the method of Huston and McBride, as given in paragraph 350. In samples so rich

⁹⁸ *Berichte der deutschen chemischen Gesellschaft*, 1893, **26** : 386.

in organic matter as peat the method of Grandeau does not give good results.

Often more than half the weight of the dry substance is soluble in ammonia after treatment with acid. The nitrogen in the original sample and in the separated humus should be estimated by moist combustion with sulfuric acid in the usual manner

538. The Mineral Contents of Humus.—The material obtained by precipitating the alkaline extract of a vegetable earth with an acid does not consist alone of oxygen, carbon, hydrogen, and nitrogen. The complex molecules which make up this mixture contain certain quantities of iron, sulfur, and phosphorus in an organic state. These bodies are left as inorganic compounds on ignition, provided there is enough of base present to combine with all the acid elements. Much of the sulfur and phosphorus, however, in these compounds might be lost by simple ignition. In such cases moist oxidation of these bodies must be practiced, or the gases of combustion passed over bodies capable of absorbing the oxidized materials in order to detect and determine them. The proper methods of accomplishing this have already been pointed out for vegetable soils, and the same processes are applicable in the case of extracted and precipitated humus.

Another proof that both phosphorus and sulfur are present in humus in an organic state is found in the fact pointed out by Eggertz and Nilson, that the ash of peat soils is always richer in sulfuric and phosphoric acids than the solution obtained therefrom by hydrochloric acid.⁸⁵

In a sample of peat examined by them there was found in the ash 1.46 per cent SO_3 , and in the acid extract only 0.05 per cent SO_3 ; and in the ash 0.3 per cent P_2O_5 , while in the extract only 0.03 per cent P_2O_5 .

539. Combustion of the Humus.—The percentage composition of the extracted humus can be determined, after drying to constant weight, by combustion with copper oxid. There is little use in trying to assign definite chemical formulas to any of the components of the complex which we call humus. Some of the sup-

⁸⁵ Biedermann's Central-Blatt für Agrikultur-Chemie, 1889, 18 : 664.

posed formulas which have been given (page 53) cannot, in the light of our present knowledge, be regarded as of any value.

540. Ether Extract.—Most peaty soils, when very dry, are not easily moistened with water. This is due to a superficial coating of fatty or resinous bodies which prevents the water from reaching the particles. In such cases water will pass between the particles and percolate to a considerable depth, but without wetting. This oily matter can be removed by treating the dry material with ether in any approved extraction apparatus. For the separation of the more purely fatty bodies, light petroleum may be used, while the total of such matters is extractable with sulfuric ether. The extracted bodies should be examined to determine their nature, whether fatty or composed of other materials soluble in ether. The quantity of this material in some peat soils is remarkably high. In a Florida peat, examined in the laboratory of the Bureau of Chemistry, 18.95 per cent of the air-dried substance, which contained still 41.83 per cent of water, or about 32.5 per cent of the water-free material were found to be soluble in ether.

The color of the ether extract may be almost black, showing the extraction of a part of the humus or coloring matter in the peat. This extractive coloring matter may also be a partial oxidation product of the original chlorophyll of the plant.

541. Further Examination of the Ether Extract.—The ether extract should be first treated with petroleum ether, unless this substance be used first in extraction. Afterwards, it is to be exhausted with strong alcohol, and the quantities of material soluble in the three reagents separately determined.

The nitrogen is further to be determined in the several extracts, and, for control, in the residue of the peat.

The method of procedure practiced in the laboratory of the Bureau of Chemistry is to first extract the sample with petroleum ether, which will yield any free fat acids, fats, or oils, waxes, and possibly some resinous matter. A weighed portion of the sample, about two grams, is extracted quantitatively by one of the methods which will be described in the second volume of this manual.

From two to five kilograms of the sample are then extracted

in bulk for the purpose of securing a sufficient quantity of the material to use for further analysis.⁹⁶

In each case the petroleum is followed by sulfuric ether, and in this way the chlorophyl, resins, etc., are obtained. This extract is examined also for its several proximate constituents.⁹⁷

The treatment with ether is followed by extraction with absolute alcohol for the removal of tannins and other glucosides, resins insoluble in ether, etc., and the extract subjected to the usual examination. Instead of absolute alcohol a spirit of 95 per cent strength, or even of 80 per cent may be used. The final residue should be subjected to the usual determination for nitrogen, volatile matter, ash, etc., in the manner already described. The large amount of resinous and other matters soluble in petroleum and ether, which is found in the Florida peat soils, is probably due to the proximity of pine forests, the debris of which, sooner or later, find their way to these lacustrine deposits. Considerable portions of organic humic acids and even humus itself, may also be removed by ether and alcohol and in every case the nitrogen should be determined in these extracts.

542. Examination of the Acid Extract of Humus Soils.—Forster calls attention to the difficulties attending the analysis of the acid soluble constituents of soil.⁹⁸ Among these are mentioned the difficulty of washing out of the acid insoluble residue all dissolved material, particularly from clay or humus soils. The separation of the alkali earths and the alkalies from the voluminous iron and alumina precipitate is intricate and time consuming. Not less unsatisfactory is the separation of manganese by the usual methods.

As an improvement of the usual procedure, the author offers the following:

Solution in Ten Per Cent HCl.—From 100 to 200 grams of air-dry fine material are treated in a flask with ten per cent hydrochloric acid in the proportion of one gram of soil to two cubic centimeters of ten per cent acid. After removing carbon dioxide with a current of air, the flask and its contents are weighed and the mixture heated on the water-bath for three hours. After cooling,

⁹⁶ Dragendorff, *Plant Analysis*, London, 1884 : 8.

⁹⁷ Dragendorff, *Plant Analysis*, London, 1884 : 31.

⁹⁸ *Chemiker Zeitung*, 1894, 14 : 36-38.

the evaporated water is restored and the whole so diluted that for each gram of soil there shall be ten cubic centimeters of solution. Filter through a dry filter, evaporate from 800 to 1,600 cubic centimeters of the filtrate with from five to ten cubic centimeters of nitric acid to dryness; take up in hydrochloric acid and water and dilute so that each 100 cubic centimeters shall equal 40 or 50 grams of air-dry soil. This solution is used for the subsequent determination of potash, lime, magnesia, phosphoric acid and sulfuric acid.

Determination of Potash.—An aliquot part of the solution equal to from 20 to 50 grams of air-dry soil is evaporated to dryness in a platinum dish, ignited below redness and distilled water and a little hydrogen peroxid added to oxidize iron. To the hot solution add an excess of ammonium carbonate, filter, wash with hot water, and evaporate the filtrate to dryness, heat in air-bath one-half hour, then at 150° , and finally ignite below redness. Dissolve the residue in a little water, add sufficient barium chlorid solution and a drop of hydrochloric acid and again evaporate. Dissolve in water, and after filtering, determine potash with platinic chlorid as usual.

Determination of Phosphoric Acid.—An aliquot part of the solution equal to from 20 to 50 grams of air-dried soil is neutralized with ammonia, heated to 80° in a water-bath and 100 cubic centimeters of ammonium molybdate added and allowed to stand 15 minutes, and then filtered. Longer heating at lower temperatures is useless and to be avoided, as thereby molybdic acid in considerable quantity and iron are precipitated along with the ammonium phospho-molybdate and the ammonium magnesium phosphate thus contaminated. The precipitate is collected on a small filter that the wash solution and ammonia required for dissolving may be limited to the smallest required amount. The subsequent formation and complete separation of the ammonium magnesium phosphate precipitate is hastened by shaking from one-fourth to one-half hour.

Determination of Lime.—A part of the solution equal to 30 grams of soil (or less of a soil rich in lime) is made ammoniacal,

heated to boiling and a boiling solution of from four to five grams of ammonium oxalate is added and the whole heated to boiling again for a few minutes. After removing from the flame the solution is immediately made acid with acetic acid. If the solution is still brown in color, or if all the iron is not dissolved, add more ammonium oxalate and place the beaker in a boiling water-bath until the solution is clear and the iron is all dissolved. The precipitation of the calcium oxalate in ammoniacal solution before the formation of ferric oxalate is necessary because calcium oxalate is not completely precipitated in acetic acid in the presence of iron. The calcium oxalate, once formed, is insoluble. Filter on a double filter, wash with hot water, dry, burn the filter over a small flame and dissolve in hot dilute hydrochloric acid in a 150 cubic centimeter flask. Evaporate repeatedly with nitric acid to break up chlorids and precipitate with ammonium persulfate in nitric acid solution according to Marshall.⁹⁹ Add ammonium phosphate to combine with iron and alumina, make ammoniacal, and after cooling, add acetic acid in slight excess. Make up to volume, filter through a dry filter, and determine calcium as oxalate, as usual, in 100 cubic centimeters of filtrate.

Or, to the hydrochloric acid solution add sufficient ammonium phosphate, an excess of pure sodium hydroxid, and ammonium persulfate, and heat to boiling for three to five minutes, cool, make up to volume and filter through a folded filter and determine lime in 100 cubic centimeters of the filtrate in the usual manner.

The precipitation of manganese is not as complete with hydrogen peroxid as with ammonium persulfate. From an ammoniacal solution manganese phosphate is not precipitated, and therefore a fixed alkali is required, instead of ammonia. The presence of chlorids does not interfere with the precipitation from alkaline solutions. From acetic acid solution manganese phosphate is not precipitated. As the quantity of manganese is small both in soils and ashes, the error introduced by the co-precipitation of other metallic oxids (lime and magnesia) is negligible.

Determination of Magnesia.—To a part of the solution equal to 30 grams of air-dry soil add an excess of ammonium phosphate,

⁹⁹ *Berichte der deutschen chemischen Gesellschaft*, 1902, 35 : 3266.

and if a precipitate forms dissolve in hydrochloric acid. The solution must be clear and colorless as the brown precipitate produced by ammonia is difficultly soluble in ammonium citrate. Add sufficient ammonia to make the whole contain two per cent, shake for from one-fourth to one-half hour, add 50 cubic centimeters of ammonium citrate solution (as used for superphosphates) and shake again for from one-fourth to one-half hour. Precipitation from solutions in which the iron is completely dissolved in ammonium citrate or tartrate gives low results, but if precipitated as above the dissolved iron is without effect. The precipitate may be contaminated with lime, iron, aluminum and manganese. Filter, and wash with ammonia, dissolve in hydrochloric acid and wash filter with hot water. To the filtrate, add excess of ammonium oxalate, make ammoniacal, boil and add acetic acid. After shaking, separate the calcium oxalate by filtration and wash the filter thoroughly. To the filtrate add an excess of ammonium phosphate and sufficient ammonia to make the solution two per cent strength. Shake one-half hour, add 20 cubic centimeters of ammonium citrate and shake again for one-half hour. The precipitate still contains traces of iron, aluminum and manganese to remove which it is ignited in a platinum crucible, dissolved in hydrochloric acid and hot water. Add sufficient ammonium phosphate, then pure sodium hydroxid, oxidize with ammonium persulfate, heat to boiling, cool, add acetic acid in excess to make up to volume in a 150 cubic centimeter flask and in 100 cubic centimeters of the filtrate, determine magnesia in the usual manner.

The above scheme presents some novel or at least little practiced methods of procedure, but with the absence of comparative data there is little evidence of any superiority in the method, either for time-saving or accuracy over the methods in common use. It is offered more as a possible base for further investigation than as a process to be implicitly followed.

543. Acidity of Peat Soils.—The acid reaction of peaty soils, especially of the high peat soils, is aside from the presence of carbon dioxid, due to the presence of free humic acids or acid humates. An exact method for determining quantitatively the

acidity of the soil is not yet known, and especially is it desirable to have a method whereby the acidity of the peat soils can be determined with satisfactory exactness. It seemed worth while to make an attempt to determine the acidity of the peat soils by exhausting them with neutral solvents, such as salt solutions, etc., and estimating them for the acidity of the extract, in order to measure in some quantity the acidity in the substances which are present. These substances have very different degrees of solubility, and in addition to this the titration of extracts obtained in this way, inasmuch as they are colored by dissolved organic bodies, is either impossible or extremely difficult. Some of these coloring matters themselves possess the quality of an indicator, and in such cases the titration is more easily accomplished. There is, moreover, a radical objection to the use of bases in the titration of acid extracts from peaty soils. Since humus bodies which are present and which are not of an acid nature, under the influence of bases and the presence of oxygen are decomposed with the formation of humus acids, this decomposition in the presence of basic bodies and oxygen takes place often with great rapidity. The faculty is ascribed to humus acids of displacing carbon dioxid from carbonates. Whether this capacity is possessed by all the humus acids, or only by some of them, is not known. Humic acids of this kind, however, must be placed in the first line of those which cause the acidity of peat soils, and to these acids are doubtless due the vigorous chemical and physiological phenomena which humus acids in general produce.

Tacke proposes to determine the total acidity of peat soils by the method which is described in paragraph 357.

The carbonate which is to be used for decomposition under the influence of the acid humates must be a neutral reacting body, so that if it is in the cold it can exert no decomposing influence upon the humus substances. The presence of oxygen, through the influence of which the decomposition of the humus substance may take place with the formation of carbon dioxid, is to be prevented, therefore the humus acids must work upon the carbonate in an atmosphere free of oxygen, or in a vacuum. On account of the difficult solubility of certain humic acids the substance must

be in its finest possible state of subdivision. The carbonate also must be in a similarly fine state of division, which is best secured by obtaining the silt through action of water, or the carbonate of lime may be used in the form of freshly precipitated lime carbonate.

RARE CONSTITUENTS OF SOILS.

544. Estimation of Copper.—The natural occurrence of copper in many vegetables has acquired additional significance by reason of its relation to the copper which may find its way into cultivated soil from the large quantities of copper compounds used as fungicides. Copper cannot be regarded, in any sense, as a plant food. It can only be considered as an accidental and non-essential constituent of vegetable matter. It is by no means certain, however, that copper may not be, in some sense, in organic combination, as phosphorus and sulfur often are. It is said to be found in certain animal organisms, notably in the oyster. In the estimation of soluble copper in soils, there is first made a hydrochloric acid solution of the sample. The solution is treated with well-washed hydrogen sulfid until saturated. The precipitate is collected at once on a gooch, washed with water containing the precipitating reagent, dried, gently ignited or roasted, and dissolved in aqua regia. After evaporating to dryness on a steam-bath, water and hydrochloric acid are added, and the copper reprecipitated in the manner described above.

If zinc be present in the sample the solution should be made very strongly acid with hydrochloric before the treatment with hydrogen sulfid, otherwise some zinc may be carried down with the copper.¹ If lead be present it is also precipitated with the copper and can be separated as described below. The precipitate is treated as above and in the filtrate from the solution in nitric acid after the second precipitation the copper is precipitated as hydroxid by potash, collected in a porcelain gooch, dried, ignited, and weighed as CuO . Or the copper may be secured as sulfate and estimated electrolytically in the manner described in volume third for the gravimetric estimation of sugar. In very minute

¹ *Journal für praktische Chemie*, 1858, **73** : 241.

quantities copper may also be determined colorimetrically as follows:

The previous separation of the copper by the process described above is often unnecessary and the determination may be accomplished directly as follows:

Evaporate the soil solution containing the copper to dryness and digest on the steam-bath for one-half hour with nitric acid, evaporate to dryness with the addition of one cubic centimeter of concentrated sulfuric acid and heat until white fumes are given off. Digest on the steam-bath with 25 centimeters of water and a few drops of nitric acid, filter and precipitate the copper by electrolysis. Dissolve the copper from the electrode with nitric acid and evaporate. Dissolve in water with the addition of one drop of nitric acid. If there is sufficient copper present it is estimated gravimetrically or by titration. If there are only a few tenths of a milligram it is determined by the colorimetric method which is as follows: In a large nessler cylinder place five drops of potassium ferro-cyanid, add the copper solution and five cubic centimeters of ammonium nitrate. The color is then compared with a cylinder filled in the same way with a solution containing a known amount of copper.

545. Estimation of Lead.—If the soil contain lead this metal will be thrown down with the copper as sulfid in the manner described above. In this case the mixed sulfids are dissolved in nitric acid, diluted with water, filtered, and the filter well washed. The filtrate is treated with sulfuric acid in considerable excess, and evaporated until all the nitric acid has passed off and the sulfuric acid begins to escape. After cooling, water is added and the lead sulfate collected on a porcelain gouch and washed with water containing sulfuric acid. Finally it is washed with alcohol, dried, ignited, and the lead weighed as $PbSO_4$.

546. Estimation of Zinc.—If zinc be present in the hydrochloric acid extract of a soil it may be estimated as carbonate after freeing it carefully of iron. The principal part of the iron should first be separated in the usual way by sodium acetate. In the warm solution (acid with acetic) the zinc is precipitated by hydrogen sulfid in excess. The beaker in which the precipitation

takes place should be left covered in a warm place at least 12 hours. After collecting the zinc sulfid on a filter it is washed with water saturated with hydrogen sulfid. In order to free the zinc from every trace of iron it is better to dissolve the precipitate in hot dilute hydrochloric acid and reprecipitate as above, and, after boiling with some potassium chlorate, saturate it with ammonia. Any remaining trace of iron is precipitated as ferric hydroxid while the zinc remains in solution. The ferric hydroxid is separated by filtration and the filtrate, after acidifying with acetic, is treated with hydrogen sulfid as above. The zinc sulfid is dissolved again in hot hydrochloric acid, oxidized with potassium chlorate, the acid almost neutralized with soda and the zinc precipitated as carbonate with the sodium salt. After precipitation, the contents of the beaker are boiled until all free carbon dioxide is expelled, the carbonate collected on a filter, washed with hot water, dried, ignited, and weighed as ZnO.

547. The Occurrence of Strontium in Soils.—Strontium, though chemically associated with calcium by reason of their class and reaction similarities, is not generally recognized as a constituent of the ash of plants, and therefore is not regarded as a soil constituent. Its occurrence in certain barks has been pointed out by Trimble.² The barks examined were chiefly of the genus *Castanopsis* and two oaks from Singapore. The ash of these samples yielded notable quantities of strontium. Whether strontium can replace lime in any of the functions of plant growth has not been determined. Its presence appears more likely to be due to local causes.

When strontium is found in the ash of plants, it may be separated from calcium in the course of analysis by the usual process.

The strontium is precipitated with the calcium as oxalate. The precipitate is ignited, dissolved in hydrochloric acid, boiled with ammonia to separate any traces of iron or alumina, and after filtering reprecipitated with ammonium oxalate. The precipitate is ignited, finally over the blast until the oxids are formed, dissolved in nitric acid, evaporated to dryness and heated to 150° and the nitrates separated either by ether-alcohol,³ or by amyl-alcohol.⁴

² American Journal of Pharmacy, 1897, 69 : 296.

³ Zeitschrift für analytische Chemie, 1893, 32 : 189 and 312.

⁴ American Journal of Science, 1892, [3], 16 : 50 and 314.

548. Boric Acid.—Boron, while not regarded as an essential plant food, is found quite uniformly in the ashes of a large number of plants. It may, therefore, be of some interest to the agricultural analyst to determine if any of its compounds be present in a soil extract or mineral water. For this purpose the following method may be employed. To one liter of the water or soil solu-

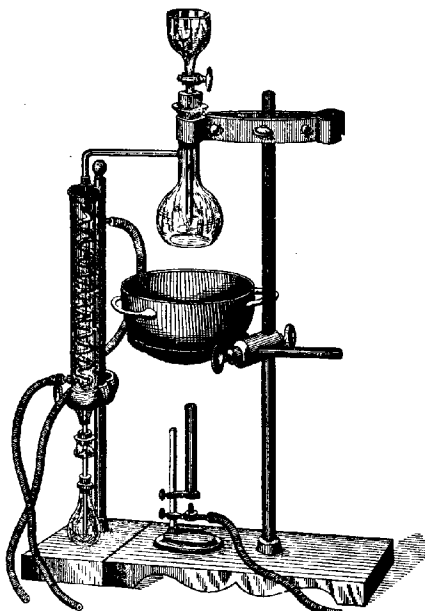


Fig. 92. Apparatus for Boric Acid.

tion supposed to contain boric acid add enough sodium carbonate to produce distinct alkalinity. After evaporation to dryness acidify the residue with hydrochloric acid, apply a piece of turmeric paper and dry at a moderate heat. The development of a brown-red tint will reveal the presence of boric acid.

The qualitative method suggested by Howard⁵ for the detection of minute quantities of turmeric in mustard has been employed by

⁵ Science, 1904, 19 : 583.

Bigelow and Brinton under carefully controlled conditions for the quantitative estimation of boric acid in minute quantities. This method may be applied to a soil solution as follows.

One or two liters of the solution are made slightly alkaline by means of lime water, evaporated to dryness and ignited. The residue is then dissolved in a small amount of water, the solution diluted to a convenient volume, and an aliquot portion, about ten cubic centimeters transferred to a platinum dish, and treated with one cubic centimeter of concentrated hydrochloric acid.

A strip of turmeric paper 15 millimeters wide and 250 millimeters long, prepared by dipping strips of porous filter paper into a solution of 50 cubic centimeters of curcumin in 100 cubic centimeters of alcohol, and drying, is then suspended with the lower end dipping into the top of the solution. The boric acid is carried up by capillarity and concentrated in a zone just below the highest point at which the paper is wet by the solution.

The maximum color is obtained by this method in about four hours, and is compared with solutions containing known amounts of boric acid and treated in the same manner. This method, as applied by Bigelow and Brinton to solutions of boric acid varying from one part in 100,000 to one part in 1,000,000, determines these minute quantities with a fair degree of precision.

Only bohemian glassware should be used in preparing the solutions since other varieties often contain boron as a constituent.

The quantitative estimation of the acid when present in notable quantity is accomplished as follows:⁶ One or more liters of the water or soil solution rendered alkaline by sodium hydroxid and then acidified by nitric or acetic acid are evaporated to dryness in the distillation flask, shown in Fig. 92. About one gram of recently ignited pure lime, cooled in a desiccator and weighed accurately, is introduced into the receiving flask at the bottom of the condenser and slaked by a few cubic centimeters of water. When the flask is attached, the terminal tube of the condensing apparatus should dip into the lime-water in the receiving flask. The heating-bath is partly filled with paraffin at a temperature of about 120°. After cooling somewhat, ten cubic centimeters of methyl-alcohol are introduced into the distillation flask by means

⁶ Gooch: American Chemical Journal, 1887, 9 : 23.

of the stoppered funnel-tube. The paraffin-bath is raised so that the entire bulb of the flask is immersed therein and the distillation continued until all the liquid has been distilled. This operation with methyl-alcohol is repeated five times. The boric acid passes off with the distillate and is found in the flask below the condenser as calcium borate. The contents of the distillation flask are evaporated to dryness and ignited conveniently in the same crucible in which the lime was burned. The increase in weight represents the quantity of boric anhydrid, B_2O_3 , obtained.

549. Method of Moissan.—The principle of the method of Gooch which has just been described, is applied by Moissan in a slightly modified manner.⁷

In this method the generating flask is made smaller than in the gooch apparatus, and the funnel at the top is oval and provided with a ground-glass stopper. It is closed at the bottom with a glass stop-cock, and the slender funnel-tube enters through a rubber stopper and ends about the middle of the bulb of the flask. The delivery-tube connecting the distilling flask with the condenser is longer than in Fig. 91, and is bent upward at its middle part in the form of an obtuse angle. The receiving flask is connected with the condenser by means of a tube-shaped funnel, which prevents any regurgitation into the generating flask. The receiving flask also has attached to it a three-bulb potash absorption tube, through which all vapors escaping from the receiving flask must pass. The bulbs contain a five per cent solution of ammonia. The receiving flask should be placed in a crystallizing dish and kept surrounded with ice-water.

The boron which is to be estimated should be in the form of boric acid. This can readily be secured by treating the residue to be analyzed with nitric acid in a sealed tube. The mixture is introduced into the generating flask, washing with a little nitric acid, and evaporated to dryness. The heat is removed, and, by means of the funnel, ten cubic centimeters of methyl-alcohol added, and the distillation is renewed. This operation with methyl-alcohol is repeated four times, taking care to distill to dryness in each case before the addition of a fresh quantity of alcohol. After-

⁷ Bulletin de la Société Chimique de Paris, 1894, [3], 11 : 955.

wards, there is introduced into the apparatus one cubic centimeter each of distilled water and nitric acid and the distillation again carried to dryness. The treatment with methyl-alcohol, as described above, is then repeated three times. To determine whether all the boric acid has passed over, the receiving flask at the bottom of the condenser is disconnected and a drop of the alcohol taken from the end of the condensing tube by means of a filament of filter paper. On burning, the flame should not show any trace of green. In case a green color is observed, the distillation with nitric acid and methyl-alcohol must be repeated.

The ammonia in the potash bulbs serves to arrest any of the vapors carrying boric acid which might escape from the receiving flask. The contents of the bulbs are to be mixed with the liquid in the receiving dish, and the whole poured onto a known weight of recently ignited calcium oxid contained in a platinum dish, and the mixture briskly stirred. If the liquid be very acid the platinum dish should be kept in ice-water to prevent heating. After 15 minutes the liquid usually becomes alkaline, and it is then evaporated at a temperature below the boiling-point of methyl-alcohol (66°). The mass, after the methyl-alcohol has disappeared, is dried at a gradually increasing temperature, and finally, the dish is ignited over a blast, at first covered and afterwards open. This dish is covered and weighed and again ignited until constant weight is obtained.

The lime used should be specially prepared by igniting calcium nitrate incompletely, and reigniting a portion of this to constant weight just before beginning each analysis. The calcium oxid is then obtained in a perfectly fresh state. It should be employed in considerable excess, for each half gram of boric acid at least eight grams of the lime. The operation is tedious but the results are quite accurate.

550. Volumetric Estimation of Boron.—The gravimetric determinations, described above, are time consuming and successful efforts have been made to substitute volumetric processes therefore. The best of these methods is based on the process described by Jones,⁸ which depends on the titration of the boric acid in

⁸ American Journal of Science, 1899, [4], 7: 147.

presence of a carbohydrate. A clearer acid reaction is thus manifested which renders the indicator more accurate and satisfactory.

Glycerol has the same effect and is the best material for sharp reactions, except for the impurities it may contain. For general purposes mannite is to be preferred.

The method of procedure is that described in Sutton's Volumetric Analysis.⁹ The soil solution containing boric acid after the removal of the phosphoric acid is evaporated to dryness after being made alkaline, ignited to destroy organic matter, the ash dissolved in dilute acid, again rendered alkaline, filtered, and the boric acid determined in the filtrate after neutralization and the addition of mannite. None of the methods given above, except the turmeric paper process, is of value unless the quantity of boric acid amounts to at least one-tenth of one per cent, which is rarely the case with soils.

551. Occurrence and Determination of Titanium in Soils.—The disturbing effects of the presence of titanium in the analysis of soils has not been noticed by agricultural chemists until recently. West has called attention to the presence of titanium in the ashes of many plants and infers that it is an element very commonly absorbed by growing vegetation.¹⁰ It is found in the ash of oak and apple wood, in apples, cow peas and cottonseed meal. It is also found in bituminous and in large quantities in anthracite coal. The wide distribution of titanium in the soil is not surprising when its common occurrence in minerals and rocks is taken into consideration.¹¹ The titanium, which is of interest to the soil analyst, is that found in solution with the iron and alumina.

On account of the great insolubility of titanium phosphate some care is required to separate the titanium when iron, alumina and phosphoric acid are found in hydrochloric acid solution of the soil.

To separate the titanium the modified method of Baskerville, as described by Bain may be used.¹² The acid is neutralized by ammonia and saturated with sulfurous acid and boiled for three

⁹ Sutton's Volumetric Analysis, 1904, 9th edition, 94.

¹⁰ Journal of the American Chemical Society, 1896, 18 : 403.

¹¹ Clarke and Hillebrand, Bulletin No. 148, United States Geological Survey, Washington, 1897, 65 et seq.

¹² Journal of the American Chemical Society, 1903, 25 : 1081.

minutes to precipitate the titanium dioxid. The precipitate is dissolved in hydrochloric acid 1:1. Any flocks of titanium phosphate which resist solution are digested with the hot acid until finally dissolved. The solution is again neutralized with ammonia and the titanium dioxid again precipitated by sulfurous acid. If not pure white the precipitate is collected and fused with sodium carbonate and the melt dissolved in sulfuric acid. Any insoluble residue is subjected to the same treatment as above, and the whole solution, after suitable dilution, treated with ammonia in excess. The precipitate is collected, dissolved in hydrochloric acid, neutralized with ammonia and precipitated with sulfurous acid. The titanium dioxid is collected, dried, ignited, and weighed. The substance as thus prepared still contains a trace of iron. For a more detailed description of the approved methods of separating and determining titanium Bain's article cited above may be consulted. The colorimetric method of determining titanium is described in paragraph 436.

552. Method of Pellet and Fribourg.—Pellet and Fribourg have studied very carefully the influence of titanium upon the determination of alumina in the presence of oxid of iron and of phosphoric acid and have suggested some slight modifications in the methods of preparing the soil solutions for determination.¹³

The investigations which have been made refer also to the determination of titanium in the ashes of vegetable substances in quantities where the amount is less than .2 of one per cent. In the preparation of the solution for analysis 30 grams of hydrofluoric acid are placed in a platinum capsule and in small quantities there is added a quantity of about three grams of dry, finely pulverized soil, and finally three cubic centimeters of pure sulfuric acid, and the mixture evaporated on a sand bath. The residue is lightly ignited just to reach complete dryness but not sufficient to decompose the sulfates which are formed. The mass is coarsely pulverized with a spatula and mixed with 15 grams of bisulfate of potassium and fused.

After cooling, the mass is detached from the platinum dish and coarsely pulverized, dissolved in from 200 to 250 cubic centimeters of water at a temperature of 60 degrees, cooled, the volume completed to 300 cubic centimeters, filtered, in order to

¹³ *Annales de Chimie analytique*, 1905, 10 : 413.

separate any traces of sand, and 250 cubic centimeters of the filtrate, that is, an amount corresponding to 2.5 grams of the soil, are placed in a flask of 400 cubic centimeters capacity.

Forty cubic centimeters of the residue of the filtrate are titrated with a solution of potassium hydroxid of a strength sufficient for ten cubic centimeters thereof to neutralize five grams of potassium bisulfate. To the 250 cubic centimeters of the filtrate there is then added a quantity of potassium hydroxid sufficient to neutralize all the potassium bisulfate therein, except five grams. There is finally added a solution of sulfurous acid of 1020 to 1025 density freshly prepared, the solution boiled for two hours, and during the boiling there are twice added 50 cubic centimeters of the sulfurous acid solution.

The contents of the flask are then put upon a filter and washed with boiling water, dried and burned. This precipitate is almost pure titanic acid, containing only a little phosphoric acid. It is remelted with two grams of carbonate of potash, taken up with boiling water and filtered, and washed with a two per cent solution of carbonate of potash. The titanic acid then remains in the form of insoluble titanate. A very small portion passes into solution and this error is corrected by determinations with known quantities of pure titanic acid. The insoluble titanate is burned, afterwards melted with one gram of bisulfate of potassium and reprecipitated, as described above. The TiO_2 obtained is ignited and the quantity obtained is added to that found by fusion with the carbonate of potash.

In the estimation by the colorimetric method, half a gram of soil or 2.5 grams of ash are treated with hydrofluoric acid, as described above. The residue is detached from the platinum capsule, which is easily accomplished, pulverized with a spatula and mixed with five grams of bisulfate of potash, fused, taken up in distilled water containing 15 per cent of pure sulfuric acid at a maximum temperature of 60 degrees, cooled, and the volume completed to 100 cubic centimeters. Of this quantity from one to ten cubic centimeters, according to the content of titanium, are made up to ten cubic centimeters with distilled water, and five cubic centimeters of hydrogen peroxid added, and the color produced compared in a colorimeter with a solution prepared with a pure solution of titanic acid containing from one-tenth to one gram of the acid per liter.

INDEX.

Absorption	125
cause	127
general method of determining	316
importance	132
method of determining	133
of heat, by soils	100
of water, by soils, determination	148-156
relative to fertility	131
statement of results	138
Absorptive power, estimation	313
oxygen and air	315
Acetic acid, solvent	387
Acid digestion, method	510
insoluble materials, determination	516
soluble materials, estimation	509
strength	388
strength, influence on digestion	389
Acidity, active	379
estimation	372
inactive	379
lime water method	376
Active calcareous substances	437
Adhesion	117, 124
method of Heinrich	124
wood and iron	124
Adobe	43, 47, 48, 49
analyses	49
soils	47
Æolian rocks	27
Air, absorption	315
action in soil making	41
Alkali, equilibrium reactions	46-47
salts, composition	46
Alkalies and alkaline earths, estimation	431
determination of total	516
Alkaline soils	43
Alumina, estimation	401, 463, 478, 511
Aluminum, microchemistry	394
occurrence and properties of	8
Ammonia, comparison of methods	509
estimation	502
formation in soil	481
magnesia distillation	503
nitrification	527
production	525
production by microbes	526

Ammonium carbonate, purity	419
chlorid, solvent	386
Apparatus for soil sampling	79
Apocrenic acid	53
Aqueous rocks	21
vapor, absorption	311
Area, effect	131
Armsby, soil absorption	129
Arnold and Wedemeyer, nitrogen method	493
Arnold, sterilizing apparatus	565
Assimilable lime, estimation	440
phosphoric acid, method of Dyer	459
Atomic weights, table of	3
Atterberg, names of silt particles	199
Autoclave sterilizer	564
Available calcareous matter, estimation	438
Azotobacter	559

B

Bacon, observations on absorption	125
Bacteria, action	39
Bain, method of estimating titanium	616
Barium, microchemistry	293
occurrence	12
Barus, theory of flocculation	192
Baskerville, method of estimating titanium	616
Beaker elutriation, comparison with Hilgard's method	260
method, comparison with Schloesing's method	263
Belgian chemists, method for insoluble residue	409
Benningen, silt analysis	211
Berlin-Schoene method	244
Bernard, calcimeter	381
Berthelot and André, amid nitrogen method	505
determination of residual water	338
loss on ignition	338
method of water determination	334
nature of nitrogen in soils	482-486
odoriferous matters in soils	94
phosphoric acid method	460
silicic acid method	475
sulfuric acid method	479
volatile compounds method	505
water in soils	334
Bigelow and Brinton, quantitative method for boron	613
digestion vessels	391
Boron, estimation in soils	612
occurrence and properties	7
volumetric estimation	615
Boussingault, method for gases in soil	320
method of determining absorption	320
Braun's separating fluid	300
Breon, method for separation	301
Brewer, chemical action	191
flocculation	191
Briggs, electrical method for moisture	343
water movement	168

Brögger, method of separating minerals	306
apparatus	306
Bulk analysis	410
Bumping, prevention	494
Byerinck, azotobacter	559

C

Cadmium borotungstate	298
Caesium, identification	516
Calcmeter, Bernard's	381
Calcium carbonate, estimation	436, 437, 438
estimation	512
microchemistry	292
occurrence and properties of	9
Caldwell, preliminary treatment of soil samples	86
Cameron and Breazeale, method for carbon	354
method for bicarbonates	579
Capillarity, descending	159
determination	158
Carbon, comparison of methods for estimating	352
dioxid, content in air	5
diffusion	327
estimation	517
estimation in soil waters	585
estimation in waters	577
solvent	386
Carbon, estimation in soils	346, 347
in soils—comparison of methods	352, 353
oxidation with chromic acid	347
oxidation with permanganate	349
properties of	5
Carbonates and bicarbonates, estimation in waters	579
Belgian method	385
deficiency	383
estimation	380
Carnot, method for manganese	445
phosphoric acid	452
Cayvan, colorimetric estimation of phosphoric acid	587
Cementation test	118-124
Centrifugal elutriator	271
Chemical analysis of soils, order of examination	331
preliminary considerations	330
Chevreul, theory of equilibrium	582
Chlorin, estimation	473, 474
estimation in water	575
Mohr's method	474
occurrence and properties of	6
Pettermann's method	474
Wolff's method	474
Chromic acid, oxidation	347
Chromium	12
Citric acid, solvent	357
Clarke, relative abundance of elements	12
Classification of soils	42
Claussen, silt analysis	209
Clay, chemical nature	254

Clay, colloidal	253
effect of non-electrolytes on suspended	182
mechanical determination	264
properties	253
suspension in water	199
Clayey soils, effect of boiling on texture	266
elutriation	261
Clays	43
Cleavage of soil particles	299
Coefficient of evaporation, determination	160
Cohesion	117
and adhesion of soils	117
Colloidal clay, estimation	253
Colloids, separation	183
suspended	182
Color of rocks	20
soil, determination	93-94
Colorimeter, for phosphoric acid	390-392
Colorimetric comparison, delicacy	588
Combustion in oxygen	351
Compact soils, treatment	89
Conductivity, estimation	116
Copper, estimation in soils	609, 610
Crenic acid	51
Crystal angles, measurement	287
Culture medium	537
on solid media	551

D

Decay of rocks	32
Deherain, drainage experiments	178
Delage and Lagatu, minerals in soils	399
Desiccation, uniform conditions	343
Descending capillarity	159
Dietrich, silt analysis	228
Dietrich's elutriator	229
Diffusion of carbon dioxide, general conclusions	329
of gases, general conclusions	329
Digestion, agitation and temperature	393
Belgian method	396
cold hydrochloric acid	397
dilute hydrochloric acid	394
German method	396
method of Official Agricultural Chemists	393
Moore's method	395
of soil, Hilgard's method	392
of soils, summary of methods	399
vessels	391
Dilution method	553
trials	555
Dobeneck, method of determining absorption	316
Drainage, influence	140
waters, importance of analysis	180
Durham, suspension of clay	190
Dyer, assimilable phosphoric acid	459
method of solution	387

E

Earth worms, action	38
Elements, properties of	3
relative abundance	12
simultaneous estimation	477
Elutriating tube, influence of size	357
Elutriator, centrifugal	271
Hilgard's	247
Eruptive rocks	29
Evaporation, coefficient	157, 160
method of Wolff	162
water-free atmosphere	162
Extraction methods, comparison	388

F

Ferric oxid, alumina and phosphoric acid, collective, estimation	511
estimation	512
Filters for turbid solution	194
Fine sands, separation	225
soil, capacity for holding water	148
Fleischer, method for sulfur in peat soils	598
Flocculation	124, 184
effect of chemical action	191
illustration	184
Floccules, destruction	189
Fluoric acid, method for alkaline earths	437
Fluorin	13
occurrence and properties of	8
Frankland, Percy and Grace, views on nitrification	543
Frear, method of determining soil temperatures	111
Freezing and thawing	33
French experiment station, phosphoric acid method	485
method for lime	434
official methods, potash	413
Fuelling, method for absorption	151

G

Gases, collection	321
estimation in soils	320
in soil	311
in soils, method of study	312
passage through the soil, determination	145
relation to soil composition	311
relation to soil composition	210
Gasparin, silt analysis	225
Gawabowski, silt analysis	547
Gelatin, culture	543
mineral	420
German experiment stations, potash methods	34
Glaciers, action	53
Glucinic acid	613
Gooch, estimation of boron	465
Goss, phosphoric acid method	357
Grandeau, estimation of humus	

H

Halle experiment station, citrate method	453
lime method	441
Hands, sterilization	560
Hannen, diffusion of carbon dioxide in soils	347
Harada, apparatus for separating minerals	305
Haywood, method of water analysis	578, 579
Heat	99, 100
Heinrich, determination of passage of gases through soils	163
method for absorption	156
method of determining cohesion	124
Henrici, determination of water capacity of soils	156
Hilgard, alkaline soils	45
digestion vessels	391
humus estimation	358
hygroscopic estimation	312
method for soil analysis	400
method for soil solution	392
method of digestion	392
method of silt analysis	246
method of tabulation	274
methods of analysis of soil extract	400
nitrogen method	489
phosphoric acid method	462
practical applications	189
preliminary examination of soils	86
surface tension	187
Hilgard's elutriator	247
method, comparison with Osborne's	260
Hillebrand, mineral analysis	412
Hopkins, acidity method	375
method of tabulation	274
Howard, qualitative test for boron in soils	612
Humic acid, estimation	365
salts	55
Humus	51, 52, 53, 54
artificial	54
combustion	602
comparison of methods	362
composition	56
estimation	357, 517
German method	397
in peat soils	600
method of Pasturel	370
method of Raulin	368
method of van Bemmelen	366
official method	365
summary of results	364
ether extract	603
functions	58
influence of temperature	57
mineral contents	602
nitrogen, determination	517
soils, acid extract	604
Huston and McBride, humus method in peat soils	601

Huston and McBride, modification of Grandeau's method	359
Huston, method of determining soil absorption	137
Hydrochloric acid, solvent	388
treatment of soil with cold	397
Hydrofluoric acid, solvent	398
Hydrogen, estimation of organic	356
occurrence and properties	6
Hygroscopic coefficient, determination	312

I

Ignition, determination of loss	337
Indiana experiment station, lysimeter	176
Insoluble residue, analysis	408
Belgian method	499
Wolff's method	408
International method for potash	427
Interstitial space, volume	143
Iron and alumina, estimation	404, 409
precipitation	404
separation from phosphoric acid	587
Iron, estimation	447, 449
French method	447
method of Sachse and Becker	449
microchemistry	294
occurrence and properties of	11
Italian chemists, sulfuric acid method	473
Italian experiment stations, iron determination	449
method for potash	422

J

Joffre, action of superphosphates	584
Jones, volumetric method for boron	615

K

Kaolin, estimation	478
Kedzie, digestion vessels	391
influence of drainage	140
King and Whitson, colorimeter	592
King, aspiration apparatus	146
apparatus for soil sampling	79
capillary movement of water	167
methods of water movement	165-167
Kjeldahl, nitrogen method	489, 491, 493
Klein's separating liquid	298
Kuehn, silt analysis	203
silt cylinder	203
Knop, loss on ignition	337
method of determining soil absorption	136
silt analysis	204
Knop's silt cylinder	205
Knoerr, carbon dioxide apparatus	380
König, loss on ignition	338
Kostychoff, origin of humus	51

L

Lagatu and Delage, minerals in soils	399
Lang, specific heat method	108, 110

Lateral capillary flow	167
Latitude, affecting decay	35
Lead, estimation in soils	610
Lepière, colorimetric estimation of phosphoric acid	587
Lime, estimation	402, 407, 434, 439, 440, 441, 512
assimilable	440
estimation in humus soils	605
of active	438
of available	438
French method	434, 436
method of Halle station	441, 442
quantity to add	372
Lincoln and Barker, colorimetric estimation of silica and phosphoric acid	588
Lipman, azotobacter Byerinck	559
Lithium, identification	292
microchemistry	292
Litmus solution, preparation	497
Loams	42
Loges, humus estimation	367
Loose soils, treatment	88
Loughridge, strength of acid and time	389
Lysimetry	164, 171

M

MacBride and Huston, humus method in peat soils	601
Magnesia, estimation in humus soils	606
method of Halle station	444
Magnesium, estimation	405, 407, 443, 444, 512
Magnesium, microchemistry	293
occurrence and properties	9
Magnet, separating minerals	308
Manganese, estimation	405, 445, 511
French method	445
occurrence and properties	12
Merls	43
Masure, silt analysis	230
Mayer, method for absorption	150
modification of Shōne's method	241
Mechanical analysis, general principles	181
purpose	181
tabulation	274
Mesinger, method for carbon	356
Metamorphic rocks	28
Microchemical reaction	291
examination of silt	290
Microscope	283
Microscopic apparatus	567
Microscopical examination	283
structure of rocks	17
Mineral fragments, abundance	309
gelatin. preparation	543
sections, machine	295
Minerals, classification	15
in soils, Delage and Lagatu	309
original in rocks	16
machine for making sections	295

Minerals, secondary in rocks	16
specific gravity	296
Mineralogical examination of silt separates	281
Moissan, estimation of boron	614
Moisture, effect on soil temperature	100
electrical methods	343
estimation	599
general conclusions	344
Mondesir, apparatus for calcium carbonate	437
Moore, apparatus for digestion	394
method for potash	429
method of digestion	395
method of silt analysis	207
Muck	49
Mulder, humic acid	53
Müller, method of absorption	135
method for carbonates	383
method of determining soil absorption	135
nitrogen method	491
soda-lime method	499
Müntz, humic acids	366

N

Nefedof, silt analysis	226
Nitrates, soda-lime methods	498
in soil, estimation	487
Nitric acid, development	521
estimation in soils	569
extraction from soil	571
solvent	398
Nitric and nitrous acids, classification of methods of estimation	569
relative merits of methods of estimation	570
Nitric ferment, solation	551
Nitric nitrogen, estimation	534
Nitrification, apparatus and manipulation	537
chart	534
determination of progress	532
effect of acidity	535
effect of potassium salts	524
first reference to by Agricultural Department	521
general conclusions	568
necessary conditions	522
preparation of seed	538
statement of results	548
test of commencement	538
variation of conditions	558
Nitrifying organisms, action	40
activity	528
classification	557
depth found	540
determination of distribution	539
microscopic examination	550, 554
occurrence	536
Nitrifying power of soils, determination	543
Nitrifying solution, preparation	546

Nitrogen, active soil	486, 489
estimation, general conclusions	507
estimation in soil	516
estimation with a trace of nitrates	516
fixation	560
in soils, classes	486
in soils, estimation	480, 488, 489, 491, 494
in soils, nature	482
occurrence and properties	7
sources in soil	521
volumetric estimation	500
Nitrous acid, development	521
estimation in soils	569
Nitrous and nitric acids, production	524
nitrogen, testing	532
organisms, isolation	541, 547
Nitrous nitrogen, estimation	533
Norbel, silt analysis	227
apparatus	227
Norwacki and Borchardt, auger for soil sampling	81

O

Odor, determination	94, 95
Official Agricultural Chemists, latest methods	508
methods of analysis of soil extract	508
methods of soil solution	510
nitrogen method	489
Organic carbon, estimation	345, 346
hydrogen, estimation	356
matter, destruction	401
influence on absorption	132
quantity	346
removal	132
nitrogen in soil	519
oxygen, estimation	357
Origin of soil	32
Orth, classification of soils	198
Osborne, method of tabulation	274
modification of Schöne's method	242
silt analysis	212
Osborne's method, comparison with Hilgard's	260
Schloesing's	262
Oxalic acid, purification	418
Oxidation, order	526
Oxygen, absorption	315
estimation of organic	357
properties of	4

P

Packard, method of separating minerals	303
Pasturel, humus method	370
Peat	49
soils, acidity	607
carbon and hydrogen	598
formation	596
sampling	595

Peat soils, special treatment	594
volatile and organic matter and ash	598
water content	596
Peligt, preliminary treatment of samples	90
Pellet and Fribourg, method of estimating titanium	617
Percolation, measurement of rate	171, 176
Permeability, determination in field	163
Petermann, chlorin method	474
method for absorption	150
methods of soil analysis	406
phosphoric acid methods	458
preliminary treatment of samples	91
water in soils	335
Peters, absorption	126
Petrographic examination of silt particles	294
microscope	283
Pfaundler, method, specific heat	101-108
Phosphoric acid, Carnot's method	452
colorimetric estimation	587
estimation	407, 452, 453, 454, 455, 458, 459, 462, 465, 468, 513
in humus soils	605
in peat soils	600
in soil waters	583
etheral estimation	461
French method	455
Halle method	454
method of Goss	465
Hilgard	462
Petermann	458
provisional method	514
quantity for plant growth	585
Russin method	462
reagents for colorimetric estimation	589
separation	463, 464
volumetric method	468
Phosphorus, forms in soil	460
microchemistry	294
occurrence and properties	6
Pillitz and Zalomanoff, method	134
Polarized light, use	288
Porosity	140
determination	143
of soil to air	145
gases, determination	162
Potash and soda, estimation	515
condition in soils	412
estimation in humus soils	605
international method	427
Italian method	422
method of German experiment stations	420
Tatlock and Dyer	428
Russian method	422
selective absorption	130
Smith's method	423
soluble in cold dilute acids	415
concentrated acids	413

Potassium, estimation	403, 406, 413, 417, 420, 422, 423, 427, 428, 429
microchemistry	292
occurrence and properties of	10
permanganate, oxidation of carbon	349
Potential, effect on surface particles	185
Pure clay, properties	253
Pyrite, in peat soils	598

Q

Quincke, theory of flocculation	188
---	-----

R

Raulin, humus method	368
method for potash	420
Refractive index, determination	287
Retgers, separating liquid	301
Riga experiment station, phosphoric acid method	462
Rocks, aeolian	27
amorphous	17
aqueous	21
argillaceous	19
calcareous	19
chemical classification	19
chemical composition	31
color	20
crystalline	17
decay	32
eruptive	20, 29, 30
fragmental	17
metamorphic	28
microscopic structure	17
mineral composition	14
minerals	13
sedimentary	24
siliceous	19
specific gravity	19
stratified	19
types	17
volcanic	17
Rohrbach's solution	299
Rowland, theory of subsidence	194
Rubidium, identification	516
Russian method for potash	422

S

Saccharic acid	53
Sachse and Becker, iron method	449
Salts, preparation for absorption	139
Sample, air drying	86
preparation	508
preparation for sedimentation	269
treatment in laboratory	85, 86, 87
Samples, collecting for nitrification	539
preliminary treatment	85-92
Sampling auger	72

Sampling, conditions of success	85
for moisture	73
for permeability	73
general conclusion	91
general directions	62
instruments	72-79, 80, 81, 82, 83
method of Royal Agricultural Society	75
Caldwell	65
German experiment station	71
Grandeau	77
Hilgard	62, 63, 64
Official Agricultural Chemists	66
Official French commission	67, 68, 69, 70-87
Lawes	75
Moore	83
Peligot	71-90
Richards	64
Petermann	91
Wanschaffé	71-75, 90
Whitney	73
Warrington	539
Wolff	78-87
Swedish method	90
tubes	528
Sandstone	24
Sandy loams	42
Schlöesing and Müntz, distribution of nitrifying organisms	536
determination of CO_2	323
estimation of phosphoric acid in soil waters	584
extraction of soil waters	580
method, comparison with Osborne's	262
method of collecting gases	321, 322
method of silt analysis	216
method, statement of results	219
potash estimation	415
tube for collecting gases	320
Schoene's elutriator	231
silt analysis	231
Schreiner, colorimetric estimation of silica and phosphoric acid	587
Sedimentary rocks, classification	24
Sedimentation, acceleration	268, 270
Sediments, separation	254
weighing	256
Selective absorption of soils	130
Separation of silt particles	301
Sieve analysis, classification	198
for separating soil particles	195
method of German stations	197
Official Association of Agricultural Chemists	196
separation	195
Sifting with water	196
Silicic acid, direct estimation	475
Silica, estimation	400, 406, 410
Silicon, properties	4
Silt analysis, Belgian method	221
Benningsen's method	211

Silt analysis, Berlin-Schoene method	244
classification of results	257
comparison of methods	225
French method	216
general conclusions	275
interpretation	256
Italian method	210, 222
Mayer's modification	241
method of Claussen	206
Dietrich	228
Gasparin	210
Gawabowski	225
Hilgard	246
Knop's	204
Kühn	203
Masure	230
Moore	207
Noebel	227
Osborne	212
Schloesing	216
Schoene	231
Sjollema	273
Williams-Fadejeff	223
Wolff	207
methods	200
methods depending on subsidence	201
preparation of sample	251
separation of clay and silt	252
statement of results	209, 258
subsidence of soil particles	201
value	309
classes, illustrations	286
percentage	277
groups, measuring diameter	274
microchemical examination	290
particles, color and transparency	309
examination with polarized light	288
form and dimensions	285
microscopic examination	283
nomenclature	199
petrography	294
separation by decantation	203
separation by specific gravity	296
staining	289
separates, microscopic examination	283
Silver nitrate	300
Siphon silt cylinder	205
Size of tube, influence in silt analysis	257
Sjollema, method of separating colloids	183
silt analysis	273
Smith, method for potash	423
Soda, estimation	419
lime method	494, 498, 499
preparation	497
Sodium and potassium, estimation	403, 406
microchemical reactions	291

Sodium, occurrence and properties of	11
Soil acidity, nature	378
analysis, official methods	508
statement of results	518
absorption, importance	132
method of determining	133
capacity for water	148
chemical elements in	2
classification by sifting	198
composition, relation to gases	311
definition	1
deposition	42
dissolved matter, estimation	400
extracts, preparation	171
geologically considered	1-2
ingredients, distribution	276
gases	162
heat, sources	99
moisture	141
effect of salt solutions	170
nitrogen, active	486, 489
origin	1
particles, cleavage	290
methods of investigation	282
mineralogical examination	287
number	280
separation	195
by a liquid in motion	226
with water	196
standard sizes	195
reaction	332
samples, air drying	86
preliminary examination	86
treatment in laboratory	85
solutions, analyses	400
solvents	386
temperatures, methods of determining	110
thermometry	110
volatile compounds	505
Soils, absorptive power	125
alkaline	43
and subsoils	59
carbon dioxide	323
chemical analysis	330
elements	2
classification according to deposition	42
cohesion and adhesion	117
color	93
compact	89
conductivity for heat	116
deficient in carbonates	383
digestion with solvents	385
estimation of carbonates	380
genesis	32
loose	88
mechanical analysis	181

Soils, methods of estimating absorption of heat	116
origin	I, 32
physical properties	93
preliminary treatment	85
qualities	42
rare constituents	609
reaction	332
sampling	61
sandy	42
selective absorption	130
specific gravity	96
determination	97
solvents	385
vegetable	43-44-45-49-50
volume	97
weight of one hectare	99
Soilwater, extraction	580
Solar heat, absorption	100
Solubility, water and weak reagents	386
Solvents for soils	385
Special method, soil analysis	412
Specific gravity of soils	96-97
apparent	98
solutions	296
volumetric	98
heat of soils, determination	101
influence	100
variations	110
Spencer, photomicrographs	286
Standard sulfuric acid, preparation	49
Staining, micro-organisms	55
silt particles	286
Sterilization,	562
by heat	562
by steam pressure	562, 563
importance	560
Sterilized soil, nitrification	557
Sterilizing oven	563
Strontium, estimation in soils	611
microchemistry	393
Subcultures, method	549
Subsoil	59
Sulfur as plant food	6
estimation in peat soils	598
forms in soil	479
occurrence and properties of	5
Sulfuric acid, estimation	402, 406, 469, 470, 471, 473, 515
French method	469
Italian method	473
matters soluble	465
method of Berthelot and André	470
method of Van Remmelén	471
Surface tension	142
influence	187
theory	134
Swedish experiment station, lime method	439

T

Tacke, acidity method	373
method for acidity in peat soils	608
Tatlock, method for potash	428
Temperature, importance in nitrification	532
Texture, effect of boiling	266
Thallium nitrate	300
Thermometry	110
applications	116
method of Whitney and Marvin	112-115
stating results	111, 112
Thermostat	566
Thoulet, separating apparatus	302
solution	297
Time, influence on humus determination	362
influence on solution	389
Titanium, estimation	475, 476
occurrence and properties of	11
occurrence in soils	616

U

Ulmic acid	53
Ulmin	53, 54
Urine solution, sterilized	549

V

Vann, determination of humus	366
loss on ignition	340
water	340
sulfuric acid method	471
action	38
soils	49
Vetfeh, acidity method	372, 375, 378
colorimetric estimation of phosphoric acid	587
delicacy of colorimetric estimation of silica and phosphoric acid	588
Volatile compounds, estimation	505, 509
Volume of soil	97
Volumetric method, phosphoric acid	468

W

Wahnschaffe, sieve	196
preliminary treatment of samples	90
Walker, titanium method	476
Warrington, absorption of potash and ammonia	128
and Peake, method for carbon	347
culture medium	537
dilution method	553
Water absorption by soils, determination	148
after air drying	335
analysis, stating results	580
as solvent	386
capacity, effect of pressure	156
capillary movement	167

Water, determination	333
determination in fresh samples	333
estimation in water-free atmosphere	162
expelled at 110°	334
in fresh samples	333
in soils, drying in desiccator	334
method of Official Agricultural Chemists	336
method of König	336
movement, causes	168
effect of salts	170
methods	165
other constituents	580
residual amount, dried at 110°	338
solvent action	36
for soils	386
special examination	573
states in soil	142
Waters, estimation of total solids	574
examination of irrigation	577
methods of examination	573
sampling of irrigation	573
Way, absorptive power of soils	125, 138
Weight of soil	96
Weltschowsky, measurement of flow	173
Whitney and Marvin, method of determining soil temperatures	112
effect of potential	185
method of tabulation	274
electrical methods	343
permeability of soil	
Williams-Fadejeff, silt analysis	
machine for mineral sections	
Winogradsky, culture on mineral gelatin	
culture solution	
Wolff and Wahnschaffe, method of determination of water absorption	474
chlorin method	162
determination of coefficient of evaporation	408
method for insoluble residue	207
method for silt analysis	148
method for water coefficient	397
method of digestion	154
Wollny, determination of water absorption	587
Woodman, colorimetric estimation of phosphoric acid	12
Woodward, relative abundance of the elements	307
Wülfig, method of separating minerals	

X

Xylic acid	53
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Y

Yoder, centrifugal elutriator	271
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Z

Zinc, estimation, in soils	610
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